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Characterization and Treatment of Aqueous Wastes and Residue from Petroleum Refineries

Oklahoma State Univ., Stillwater

Prepared for

Robert S. Kerr Environmental Research Lab.
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EPA-600/2-83-089
September 1983

PB83-260281

CHARACTERIZATION AND TREATMENT OF AQUEOUS WASTES AND RESIDUE FROM PETROLEUM REFINERIES

by

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This study was conducted
in cooperation with
Oil Refiners' Waste Control Council

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16. ABSTRACT

This research project was designed to identify process wastewaters which contained a significant proportion of the total load of contaminants in petroleum refinery wastewaters and to evaluate methods for intensively treating these highly concentrated low-volume streams. In addition, selected waste residues from API gravity separator, dissolved air flotation units, and "slop" oil emulsions were analyzed to determine the presence of hazardous chemicals as listed by EPA's Office of Solid Waste.

Process wastewaters from the fluid catalytic cracking units, crude desalting unit, coking unit, and barometric condensor contained the highest levels of contaminants. These process wastewater streams were major contributors to the total load of phenol, ammonia, sulfide, and organic carbon contamination of the combined refinery wastewaters. On-site evaluations of mixed media filtration-activated carbon adsorption and a biological oxidation system indicated both systems were capable of reducing phenol, sulfide, and organic carbon levels by greater than 90 percent.

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the Nation's air, land, and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities. As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in ground water; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control, or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

The objectives of this project were to determine the raw waste load contribution of process wastes from the fluid catalytic cracking (FCC) units in a refinery and to evaluate the treatability of the FCC wastes with chemical, physical, and biological systems. Other waste streams characterized in this report are waste residues from the API separator, dissolved air flotation, and slop oil.

Clinton W. Hall

Clinton W. Hall
Director
Robert S. Kerr Environmental Research Laboratory

PREFACE

Within the past decade, the widespread use of biological treatment systems such as waste stabilization lagoons, activated sludge units, and biodisc systems by the petroleum refining industry has resulted in significant improvements in effluent quality. However, biological treatment systems may not be capable of consistantly reducing the concentration of all toxic contaminants to acceptable levels prior to discharge. Numerous investigations have demonstrated the inability of biological treatment systems to tolerate widely varying levels of toxic contaminants and still produce good quality effluents.

This project was designed to investigate methods for improving performance of biological treatment systems at petroleum refineries by reducing the total load of contaminants prior to entering the combined wastewater treatment system. The objective of this project was to identify process wastewaters which contained high concentrations of contaminants and to evaluate methods for intensively treating before discharge of these wastewaters into the combined wastewater stream. The process wastewater flows are relatively low, 50 to 200 gpm, compared to the combined flow from all sources and therefore could be treated in smaller treatment units and for longer periods of time without being cost prohibitive. Another major advantage envisioned would be a reduction in variation of load of toxic contaminants reaching the combined biological treatment system and thus fewer "upsets". A small treatment system on a process wastewater stream containing high levels of toxic contaminants followed by a biological treatment system on the combined wastewaters would also provide longer residence time for biological removal of "refractory" contaminants.

ABSTRACT

This research project was designed to identify process wastewaters which contained a significant proportion of the total load of contaminants in petroleum refinery wastewaters and to evaluate methods for intensively treating these highly concentrated low volume streams. In addition, selected waste residues from API gravity separator, Dissolved Air Flotation Units, and "slop-oil" emulsions were analyzed to determine the presence of hazardous chemicals as listed by EPA's Office of Solid Wastes.

Process wastewaters from the fluid catalytic cracking units, crude desalting unit, coking unit, and barometric condensors contained the highest levels of contaminants. These process wastewater streams were major contributors to the total load of phenol, ammonia, sulfide, and organic carbon contamination of the combined refinery wastewaters. On-site evaluations of mixed media filtration-activated carbon adsorption and a biological oxidation system indicated that both systems were capable of reducing phenol, sulfide, and organic carbon levels by >90%.

This report was submitted in fulfillment of Cooperative Agreement No. CR806798 by Oklahoma State University Water Quality Research Lab under the sponsorship of the Robert S. Kerr Environmental Research Lab, Environmental Protection Agency. This report covers the period October 1, 1979 to September 30, 1982. Work was completed September 15, 1982.

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SECTION 1

INTRODUCTION

The major objective of this project was to determine the relative contribution of aqueous wastes from fluid catalytic cracking (FCC) units to the total quantity of aqueous wastes produced within a refinery. A parallel objective was to evaluate the effectiveness of physical-chemical and biological treatment systems for intensively treating highly concentrated process unit wastewater systems.

Aqueous wastes from petroleum refineries are extremely complex and difficult to treat effectively in conventional biological systems. Operators of wastewater facilities learn through practical experience that selected process unit wastewaters can have a major influence on the effectiveness of treatment systems. Cross (1971) presented qualitative estimates of the relative contribution of process units in petroleum refineries to the overall load of contaminants in wastewaters. Catalytic cracking units were considered to be major contributors of phenol, sulfide, ammonia and alkalinity. The catalytic cracking units were considered to be moderate contributors of chemical oxygen demand and biochemical oxygen demand.

Many refineries have adopted a practice of using wastewaters from fluid catalytic cracking (FCC) units for desalting crude oil stocks. This practice reduces concentration of hydrocarbon type compounds in the FCC process wastewater by partitioning hydrocarbons between the aqueous and oily phases. In addition the total volume of water used is reduced. Most of the refineries are attempting to conserve as much wastewater as possible through recycle-reuse practices. However, complete recycle-reuse may not be economically feasible at this time. As an alternative, existing refineries may have to adopt a combination of recycle-reuse and intensive treatment of highly contaminated process wastewater streams in order to achieve 1983-85 effluent standards.

One approach which has been used by a refinery in Oklahoma for many years is to intensively treat the small volume of heavily contaminated wastewater from the FCC process unit. This refinery has been treating aqueous wastes from the coking and FCC units in an aerated lagoon prior to mixing with wastewaters from other units in the refinery for combined treatment in a series of waste stabilization lagoons. The practice has been very successful in spite of the fact that the combined treatment system of waste stabilization lagoons is generally not recognized as a highly efficient unit compared with activated sludge or physical-chemical methods such as activated carbon adsorption. However, the final effluent from this refinery has consistently been in compliance with NPDES effluent guidelines. The OSU Water Quality

Research Lab has been testing this effluent on a monthly basis since 1959 with static acute 96 h fathead minnow toxicity bioassays. In more than 90% of all the tests performed on this effluent, there was less than 50% mortality of the test minnows in undiluted effluent. In many tests, there was no mortality in the undiluted effluent. This refinery effluent has consistently been equivalent to or better than effluents from 10 other refineries with respect to toxic effects. Several of the other refiners use activated sludge or combination of activated sludge-waste stabilization lagoon treatment systems. The significantly different method of intensively treating the FCC and coking unit aqueous wastes appears to be more effective in reducing the concentration of toxic components and other wastes measured by NPDES parameters. Therefore this practice needs to be evaluated for its potential application to other refineries.

PHASES OF INVESTIGATION

Phase I (First Year)

Phase I was devoted to characterization of the influent and effluent concentration of aqueous wastes from FCC units at three refineries in Oklahoma and nearby states. The characterization phase was designed to provide quantitative information for determination of the percentage contribution of aqueous wastes from the FCC unit compared to the total contribution from all other sources within the refinery. Major emphasis was placed on measurement of significant waste components such as organic compounds, ammonia, and sulfides (Table 1).

Phase II (Second Year)

In the second year of the project, we established a small pilot-scale (0.25 gpm) dual media-activated carbon treatment system (provided by EPA lab at Ada, Oklahoma) to operate in parallel with an existing aerated lagoon system which was used to treat wastewaters from a FCC unit. A comparison of the effectiveness of the pilot-scale system with that of the full-sized aerated lagoon system was made by measuring the percent reduction in significant parameters between the influent and effluent streams. The pilot-scale system and the full-sized aerated lagoon system was sampled at six different intervals during a 30-day test period.

A second 30-day evaluation was performed after analyses of the data from the first run had been completed. This permited addition or deletion of sampling periods or parameters in order to obtain a better evaluation of the systems. In addition to the on-site evaluations, a composite sample of the effluent from the FCC unit was treated in the laboratory with ozone to determine if this method was more effective than either the dual media-activated carbon, macroreticular resin, or the aerated lagoon system. The same parameters were used in making the evaluations as in the field tests.

We recognize the inherent difficulties in direct comparisons of effectiveness of pilot-scale and bench-scale units with a full-sized aerated lagoon wastewater treatment system. However, the full-sized unit included a holding basin with 23 days retention time and an aerated basin with 6 days'

retention time, and it would have been cost prohibitive to the scope of this project to construct a pilot-scale (0.25 gpm) unit with similar retention times. Therefore, factors of scale were considered in arriving at final evaluations.

Phase III (third year)

The objective of this phase of the project was to characterize priority pollutants in residuals from the petroleum refining industry. The residuals were collected from the dissolved air flotation unit, API gravity separator, and "slop" oil residuals. The residuals were extracted by the EPA-RCRA "Extraction Procedure" for evaluation of solids to determine if they contained toxic substances (CFR 45(98)33127, May 19, 1980) and by conventional laboratory techniques.

Extracts from the residuals were analyzed for toxic heavy metals by atomic absorption spectrometry and for "priority" organic pollutants by combination gas chromatography-mass spectrometry.

SECTION 2

MATERIALS AND METHODS

SAMPLE COLLECTION

Phase I

The effluent water of petroleum refinery process units was collected by "grab" samples at 4-h intervals for a period of 24 h. The individual "grab" samples were combined to form a composite sample. The samples were collected by manual methods since electrical devices such as an automatic sample compositer were considered too dangerous to use in the process unit area of the refineries due to presence of flammable vapors. During one of the collecting trips, a fire occurred in the process unit area at approximately 7:00 p.m. Due to the potential for further fire and/or explosions, the refinery fire and safety officer would not permit anyone to enter the process unit area. We elected to use a composite of three samples collected at 4-h intervals, rather than lose the effort already expended.

During another planned collection trip, difficulties with operation of a process unit at the refinery forced cancellation of 4 h collection intervals. We elected to proceed with a single collection of wastewater samples from the process units.

The process units sampled were the crude desalting unit wastewaters, condensate of injection water from the catalytic cracking units, stripped bottoms from the sour water stripper, and condensed wash water from coking operations.

Phase II

During the on-site evaluation phase of this project, samples were manually collected from the effluent of a sour water stripper unit, an aerated pond wastewater treatment unit, and from our pilot-scale Mixed Media Filter-Activated Carbon (MMF-AC) treatment unit (Figure 1). All samples were collected in Pyrex® glass beakers and transferred to appropriate containers for preservation and transportation to lab for analyses.

Phase III

Extraction Procedures

Samples of residuals were collected from four different petroleum refineries, cooperating members of the Oil Refiners Waste Control Council.

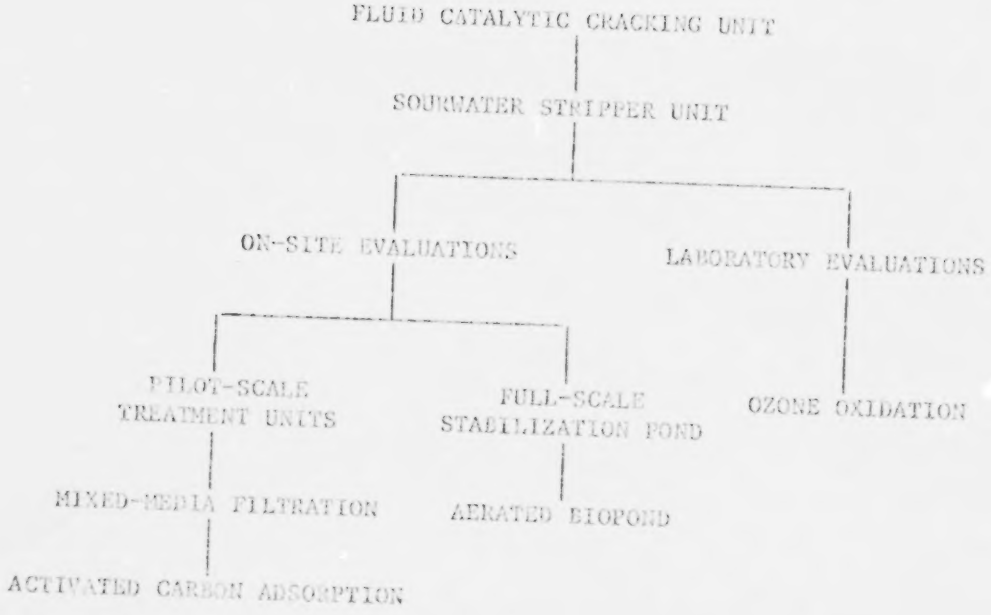


Figure 1. Schematic diagram of Phase II evaluation of treatment units.

Samples were collected and preserved in accordance with methods recommended in "Test Methods For Evaluating Solid Waste" (EPA SW-846, 1980) unless specified otherwise.

The residue samples were collected from selected locations in the wastewater treatment system of cooperating refineries, i.e. floating solids from the Dissolved Air Flotation unit, settled sludge from bottom of API gravity separating unit and, "slop oil" emulsion solids. Samples were placed in glass containers with Teflon-lined caps to prevent contamination of residuals. Collected samples were placed on ice and transported to the lab as soon as possible. Analyses were initiated within 24 h after collection.

Extraction procedures were designed to determine the potentially leachable concentration of priority pollutants in the petroleum refining residuals sampled. The EPA-RCRA Extraction Procedure (EP) was designed to measure the concentration of priority pollutants which might be leached from solids in an actively decomposing municipal waste landfill (CFR 45(98)33111, May 19, 1980). The EP utilizes a weakly acidic (pH 5) aqueous media for extraction, to simulate biogeochemical conditions which could affect migration of priority pollutants in solid waste disposal sites. The EP test was not designed to measure the total concentration of priority pollutants in solid residuals.

The extractor device was designed for complete mixing of solid with acetic acid-water media by rotating sample container 360°, with 39 complete revolutions per minute. The pH was manually checked at 15, 30, & 60 minute intervals with a calibrated pH meter, and adjusted to 5.0 ± 0.2, if necessary. The sample was rotated for 24h. After 24h, the pH was checked again and distilled water added as specified in detail in the EP guidelines. The mixture was pressure filtered through a 0.45 um Teflon® filter as previously described. A 100-ml aliquot of the combined filtrates was analyzed for soluble priority pollutant toxic metals by flame and graphite furnace atomic absorption (EPA 1979). A 1000-ml aliquot of the combined filtrate was analyzed for base-neutral and weak-acid fraction priority pollutant organic compounds by gas chromatography (GC) and combination gas chromatography-mass spectrometry (GC-MS) (SW-846).

ANALYTICAL PROCEDURES - HEAVY METALS

Sample Preservation and Preparation

Wastewater samples to be analyzed for "total recoverable" heavy metal content were placed in acid rinsed polyethylene bottles and preserved by acidification with 3 ml of concentrated nitric acid per 100 ml of sample. The sample was prepared for analysis by evaporation in a 250 ml pyrex® beaker to approximately 10 ml on a hot plate at 70°C (EPA, 1979). After evaporation the beaker was covered with watch glass and reflux digested overnight at 70°C. When digestion was complete, as indicated by absence of dark brown coloration, the sample was diluted to 100 ml with 0.2 N nitric acid, and analyzed on a Perkin Elmer Model 5000 Atomic Absorption Spectrophotometer.

TABLE 1. PARAMETERS FOR CHARACTERIZATION OF AQUEOUS WASTES FROM FLUID CATALYTIC CRACKING UNITS

Parameter	Analytical Method
Flow	Weir or estimates from pipe flow formulas
Organic Wastes	
Total Organic Carbon	Beckman TOC Analyzer
Biochemical Oxygen Demand	EPA standard bottle method
Oil and Grease	Freon extract-GC quantification
Phenolics	4-aminoantipyrine and solvent extract-GC quantification
Specific Organic Compounds	Solvent extract-GC-MS analysis
Inorganic Wastes	
Ammonia	Distillation-Titration
Sulfide	Turbidimetric
Chromium-total	Graphite Furnace Atomic Absorption
Cadmium	Graphite Furnace Atomic Absorption
Lead	Graphite Furnace Atomic Absorption
Copper	Flame Atomic Absorption
Calcium	Flame Atomic Absorption
Sodium	Flame Atomic Absorption
Potassium	Flame Atomic Absorption
Magnesium	Flame Atomic Absorption
Iron	Flame Atomic Absorption
Zinc	Flame Atomic Absorption
Nickel	Flame Atomic Absorption
Vanadium	Flame Atomic Absorption
Mercury	Cold Flameless Atomic Absorption

The preparation procedure for arsenic and selenium analyses was similar, but 3 ml of 30% hydrogen peroxide were added in the reflux digestion step. Also, the sample was evaporated to less than 50-ml and diluted back to 50 ml with distilled water. A 5-ml aliquot was transferred to 10-ml volumetric flask, mixed with 1 ml of 1% nickel nitrate solution, and diluted to volume.

The instrument was calibrated to obtain a linear regression between percent absorbance versus concentration of standard metals (Fisher Certified Standards). After calibration an EPA Quality Control Sample (QCS) was analyzed as an accuracy check. If the analyzed value of the EPA QCS differed by greater than $\pm$5% from the certified concentration, the instrument was recalibrated.

The elements sodium, calcium, magnesium, potassium, iron, copper, nickel and zinc were analyzed by flame atomic absorption using an air-acetylene fuel mixture. Lanthanum chloride was added to an aliquot of the sample prior to analyzing for sodium content, to prevent chemical ionization interference. The elements arsenic, cadmium, chromium, lead, selenium, and vanadium were analyzed with a graphite furnace on the atomic absorption spectrometer. The organic background interference was minimized with a deuterium lamp background corrector. Matrix interference was checked and corrected for by methods of standard additions in lead, arsenic, and selenium analyses.

Samples for mercury analyses were collected separately in 300-ml BOD bottles and acidified with 3 ml of concentrated nitric acid. All reagents used in preservation and analysis of mercury were certified mercury-free (Perkin Elmer Corporation). Upon return to lab, mercury analyses were performed within 24 h after collection. The analytical procedure used was the cold vapor technique (EPA Storet No. 71900); transfer 100-ml sample to 300-ml BOD bottle. Add 3 ml potassium permanganate and shake. Additional portions of potassium permanganate may be required until purple color persists for 15 minutes after shaking. Add 3 ml concentrated sulfuric acid. Shake and wait 3 minutes. Add 3 ml 1.5% hydroxylamine hydrochloride and swirl until color disappears. Wait 30 seconds. Add 3 ml 10% stannous chloride and immediately attach bottle to the aeration apparatus and measure absorbance on atomic absorption spectrometer (Perkin Elmer 306).

ANALYTICAL PROCEDURES - ORGANIC CHEMICALS

Total recoverable oil and grease analyses were performed according to the Infrared Spectrophotometric Method 413.2, EPA Methods for Chemical Analysis of Water and Wastes. Standards ranging from 25 to 200 mg/l were used. Samples were diluted, if necessary, to fall in this range. Analyses were performed on a Perkin Elmer 137 Spectrophotometer.

Phenols were determined according to EPA Methods for Chemical Analysis of Water and Wastes Method 420.1 (Spectrophotometric, Manual 4-aminoantipyrine with distillation). Analyses were performed on a Beckman DU Spectrophotometer or a Bausch and Lomb Spectronic 20.

Total Organic Carbon was determined according to EPA Methods for Chemical Analysis of Water and Wastes Method 415.1 (combustion or oxidation).

Standards ranging from 1 to 100 mg/l were used. Samples were diluted with distilled water if necessary. Analyses were performed on a Beckman Model 915 Total Organic Carbon Analyzer.

Biochemical Oxygen Demand

The 5-day BOD was performed as outlined in Standard Methods (APHA 1981). Seed dilution water was prepared from distilled water, nutrients, and microbial seed (refinery sludge). Dilutions were made according to the strength of the effluent and prior experience. A Yellow Springs Instrument Model 57 Dissolved Oxygen Meter was used for oxygen measurements.

Ammonia

EPA methods for Chemical Analysis of Water and Wastes Method 350.3 (Potentiometric, Ion Selective electrode). An Orion 407-A specific ion meter and ammonia selective electrode were calibrated with 1, 10, and 100 mg/l ammonia standards. Samples and standards were adjusted to pH >11 with 10 M sodium hydroxide immediately before analysis. Regression analysis of the standards was used to derive the sample ammonia concentrations.

Sulfide

The sulfide concentration was determined through titration with 0.1 M silver nitrate. A sulfide specific electrode on an Orion Model 407A specific ion meter was the titration end point detector. A change of potential of 300 millivolts indicated the end point.

SEMI-VOLATILE ORGANICS

Extraction of Organics

Two thousand ml of sample were extracted at pH >11 and then at pH <2 to produce a base-neutral and an acid fraction. Each extraction was performed with 800 ml methylene chloride in a continuous extractor for 24 hours. The methylene chloride extract was dried over sodium sulfate and concentrated to 1 ml.

Certain complex samples were processed by silica gel column chromotography to produce cleaner fractions. The 1 ml extract was placed at the top of a silica gel column and serially eluted with hexane, benzene, and methanol to yield aliphatic, aromatic, and polar fractions.

The various fractions were analyzed with a Hewlett-Packard 5992-B gas chromatograph-mass spectrometer (GC/MS). The GC/MS was equipped with a ®J & W DB-5 30 meter fused silica capillary column. The mass spectral identifications were performed with the aid of a printed data base (Cornu and Massot 1966) and a computer data base (NIH-EPA Mass Spectral Search System).

Quantitative analysis was performed on a Tracor 560 gas chromatograph with flame ionization detection. A J & W DB-5 30 meter capillary column was

installed for the separation of the components. Peaks on the Tracor chromatograph were identified by matching retention times and chromatographic patterns with the GC/MS chromatograph. The internal standard method was used for quantitation of identified peaks. A series of standard mixtures containing 10 to 15 compounds of interest and the internal standard (deuterated anthracene) provided response factors for parent compounds. Quantitation was performed using the response factors, and the areas of the identified peaks and the internal standard.

Solid Residues

Residues were analyzed according to the "Extraction Procedure" (EP) (Title 40, Code of Federal Regulations, Appendix II).

The residue was weighed and placed into a 1-gallon glass container with 16 times its weight of deionized water. The pH of the solution was adjusted to 5 $\pm$ 0.2 with 0.5 N acetic acid. The container was placed in a "tumbler" type extraction device. The container of water and residue were tumbled at 27 RPM for 24 hours. The water and residue were allowed to separate for 24 hours at 4°C before filtration. A portion of the water was drawn from the container and when necessary centrifuged to break emulsions. Pressure filtration through 0.45 um Teflon® filters separated the liquid and suspended solids. The filtrate was separated into several portions and analyzed for metals, phenols, ammonia, oil and grease, TOC, base-neutral organics, and acid organics.

Methods of Sample Collection

Phase 1. Evaluation of Process Unit Wastewaters

Samples of process wastewater streams were manually collected from valves in close proximity to the process unit. Hot process wastewaters were cooled by passage through a 20 foot coil of stainless steel tubing immersed in cold water bath. We planned to collect a 24 hour composite sample from each location by combining subsamples collected at 4 hour intervals. However, sampling intervals had to be modified due to a small accidental fire at one refinery and the potential for "upset" non-normal conditions in the process unit area of another refinery. Refinery management and personnel were very cooperative but understandably concerned about safety of our inexperienced staff while collecting samples in the process unit areas of the refineries.

Phase 2. On-Site Evaluations

The on-site portion of this project was performed at a cooperating petroleum refinery. A 24-foot Airstream Trailer was converted into a mobile lab containing pumps, carbon columns, mixed-media filter columns and composite sampler (Figure 1). The mobile lab was designed to permit flow through a 9" diameter by 5'-long pyrex glass column containing gravel, sand and anthrophil coal as a mixed-media filtration (MMF) unit. Flow could be directed from the MMF unit through a series of activated carbon (AC) columns consisting of four 9" diameter by 5'-long Pyrex glass columns. The carbon columns were filled with 4.5' of activated carbon thus providing 3,435 in^3 of carbon volume per column. Effluent from the carbon columns was passed through a manifold of 2-way solonoid valves controlled by an industrial

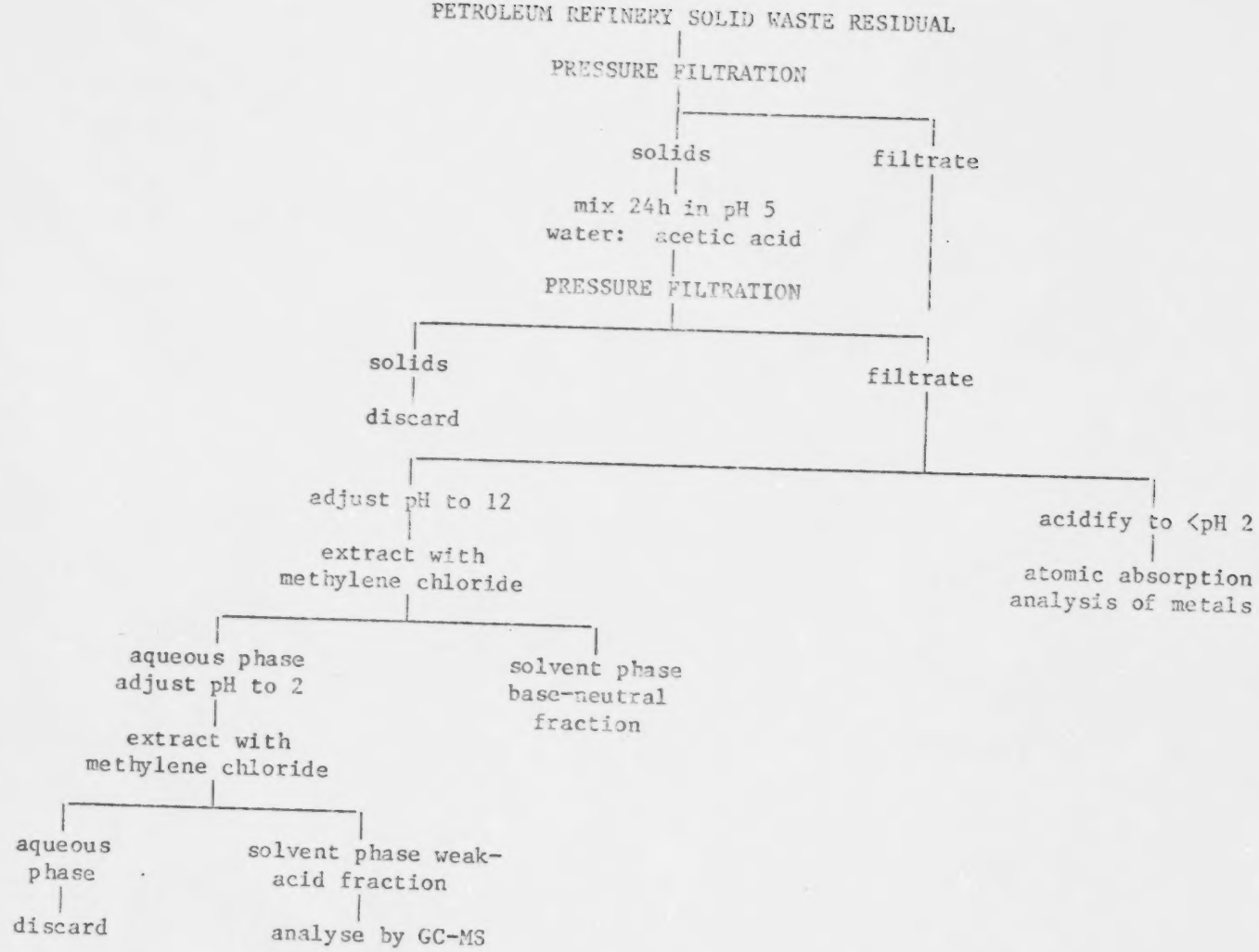


Figure 2. Proposed extraction procedures for analysis of priority pollutants in petroleum refinery residuals.

timer. The manifold allowed collection of an aliquot subsample of the carbon treated effluent by diverting flow into a composite sampling jug for 15-minute intervals every hour of the day.

During the on-site portion of this project, the mobile lab was positioned near the effluent from the sourwater stripping unit and the biopond. A 1/4" stainless-steel tubing was connected from the sourwater stripper (SWS) process wastewater to the mobile lab to provide a continuous flow subsample. The SWS effluent was too hot (80-95°C) for direct passage through the MMF-AC columns. Therefore, the SWS effluent was cooled by passing it through a 50' coil of 1/4" stainless steel tubing submerged in a cold-water bath, maintained at 5 to 10°C by a recirculating refrigeration unit (Blue M). The chilling unit was able to reduce temperature of SWS water to 25 to 30°C depending upon flow rates.

A centrifugal pump had to be installed after the cooling coil to provide enough pressure to pump SWS water through the MMF-AC units. The initial flow rate into the MMF-AC system was 400 ml/min and out of the system 150 ml/min on September 14, 1981, the starting date for the first run. Some difficulty in maintaining flow was encountered during the first run. A thick-walled Teflon tubing (1/4" OD) had been installed between the stainless steel cooling coil and the inlet from the SWS unit. The hot SWS water caused a rupture in the Teflon tubing and interrupted flow. The split Teflon tubing was repaired with new Teflon tubing, but the problem recurred. A Bevline® tubing with Teflon liner and stronger Tygon-type walls was ordered but could not be obtained before end of first run.

Originally we proposed to collect composite samples from all waste streams but due to limited flow rates through the stainless steel line, we were unable to divert part of the flow to a composite sampler without seriously impairing operation of the MMF-AC units. Therefore, grab samples were collected for the SWS and the biopond effluent. We were able to accumulate sufficient volume of sample from the MMF-AC units to composite portions of the analytical samples. However, samples for mercury, phenol, and organic priority pollutants were collected by grab sampling.

Ozone Treatment

Sour water stripper effluent from a petroleum refinery was treated with ozone in a bubble column according to the experimental procedure described below.

On the day prior to an experimental run the column was filled with tapwater and treated with ozone in order to clean it. In addition, the five-gallon effluent sample was removed from the refrigerator so that it could warm up overnight.

On the day the run was performed the column was filled with sample and the initial height of liquid recorded. The column recycle, which recirculated liquid within the column, was activated. The immersion heater located in the

bath which supplied water to the jackets on the bubble column was also activated at this time. The column was allowed to reach its operating temperature of 150°F. Thereafter, temperature was controlled at this value.

While the column was warming up, the ozonator was activated and operating conditions set at: flow -2.8 L/m; pressure -8 psig; voltage -115V. A period of at least one hour was allowed in order to reach equilibrium, and then the ozone concentration of the gas was determined (as described in the Ozone Analysis section).

Immediately prior to the run, initial samples for COD and dissolved ozone analysis were taken. Each run was initiated by directing the gas stream from the compressors into the column. Runs at high pressure (100 psig) required about five minutes to reach operating pressure. Pressure was controlled by means of a metering valve on the column off-gas line.

After the start of the run, samples were taken of the column liquid every half-hour for four hours. Those samples taken at the half-hour marks were used for dissolved ozone analysis. Samples taken on the hour marks were used for COD analysis. In addition, off-gas ozone was measured at one-hour intervals, starting at the one-half-hour mark.

After four hours the run was terminated. A final test was made of the ozone concentration in the gas from the ozonator.

Ozone Measurement

Dissolved ozone: Dissolved ozone was measured by transferring approximately 200cc of aqueous sample directly into 40cc of 10% KI solution at elevated pH. (5 drops of 5% KOH added). This solution was acidified with 10 ml of 2N H_2SO_4 and the liberated iodine titrated with standard $Na_2S_2O_3$.

Gaseous ozone: Gaseous ozone was measured by bubbling the gas stream through 600cc of 2.5% KI solution. The gas stream was then directed to a wet test meter to determine its volume.

The KI solution (containing liberated iodine) was drained from the apparatus, acidified with 10 ml of 2N H_2SO_4, and titrated with standard $Na_2S_2O_3$ to measure the iodine present.

Chemical Oxygen Demand

Chemical oxygen demand (COD) was analyzed according to the method of Standard Methods for the Examination of Water and Wastewater, XIV ed., Sec. 508-4.

SECTION 3

RESULTS AND DISCUSSION

PHASE 1. COLLECTION AND ANALYSIS OF CONTAMINANTS IN PROCESS WASTEWATERS

On April 18, 1980, we made arrangements to collect samples of process wastewaters from a cooperating petroleum refinery. We received excellant cooperation and assistance from the refinery management and technical personnel. They guided us to the appropriate areas within the process unit area to permit access to sample the process wastewater streams. In some locations, they even installed valves on process wastewater lines to permit sampling. We collected samples from 8 different locations (Table 2) within the refinery at 4 h intervals during a 24 h period of time and composited all of the samples.

The concentration of contaminants in the process wastewaters indicated that the overhead contact waters from the fluid ctalytic cracking (FCC) unit contained the highest levels of phenol, sulfide, and, BOD (Table 3). The FCC process wastewater stream also contained the second highest level of ammonia. The overhead receiving water from the coking unit contained highest levels of TOC and second highest levels of BOD. The highest levels of oil and grease detected in a process wastewater stream were from the barometric condensor.

The estimated relative contribution in pounds per day of contaminants to the combined waste load was calculated on the basis of equation 1;

1: $$\text{lbs/day} = \text{mg/l} \times \text{gpm}/448.8 \times 5.4$$

The relative percentage contribution to total waste load was calculated by equation 2;

2: $$\% \text{ of total} = \frac{\text{lbs/day of process stream}}{\text{lbs/day to API seperator}} \times 100$$

The calculated total pounds per day (Table 4) and relative percent contribution of contaminants from process wastewaters to total load in influent to API separator (Table 5) indicates that we were not able to obtain a reasonable materials balance for sulfides. Obviously, our estimates for total sulfides (lbs/day) to the API separator is much less than the contribution from individual wastewater streams numbers 1, 2, 3, and 6. Therefore, either the estimated flows are in error or there was considerable loss of sulfides from the process wastewaters prior to inlet to API separator. The calculated percent contribution of other contaminant parameters appear to be reasonable and would indicate that contact wastewaters from the FCC and barometric condensor units were major

TABLE 2. DESCRIPTION AND ESTIMATED FLOW RATES OF PROCESS WASTEWATERS SAMPLED AT REFINERY A ON APRIL 18, 1980

Sample ID	Description of Process Wastewater Stream	Volume, gpm
1	Process wastewater from overhead receiver on coking unit. Stream passed to sour-water stripper (SWS) for removal of sulfides and ammonia.	16.9
2	Process wastewater from overhead receiver on fluid catalytic cracking (FCC) unit. Stream passed to SWS for removal of sulfide and ammonia.	18
3	Stripped water from SWS.	44
4	Process wastewater from crude desalting unit.	23
5	Combined wastewaters to API separator.	270
6	Wastewater from barometric condensers.	157
7	Wastewater from caustic neutralizer. This stream is from a batch operation, approx. 14,960 gallon per month.	
8	Final effluent.	270

TABLE 3. CHARACTERIZATION OF WASTEWATERS FROM PETROLEUM REFINERY A PROCESS UNITS APRIL 18, 1980

Sample	Phenol mg/l	Sulfide mg/l	Ammonia mg/l	BOD mg/l	TOC mg/l	Oil & Grease mg/l
IPD #1	107.5	560	422	4650	1558	4028
IPD #2	477.6	1820	1307	5000	682	1530
IPD #3	271.4	800	1370	950	604	280
IPD #4	1.8	6.5	<1.0	65	76.6	700
IPD #5	125.9	9.0	438	490	697	18000
IPD #6	95.8	43.1	240	1450	330	152000
IPD #7	1.1	31.7	26.9	60	49.2	49
IPD #8	0.1	1.4	7.7	50	54.8	208

TABLE 4. CALCULATED RELATIVE CONTRIBUTION IN POUNDS PER DAY OF CONTAMINANTS FROM PROCESS WASTEWATER STREAMS TO TOTAL LOAD

Stream ID	Estimated Flow gpm	Phenol lbs/day	Sulfide lbs/day	Ammonia lbs/day	BOD lbs/day	TOC lbs/day	Oil & Grease lbs/day
1	16.9	21.8	113.9	85.8	945.4	316.8	819.1
2	18	103.4	394.1	283.1	1082.9	147.7	331.4
3	44	143.7	423.5	725.3	502.9	319.8	148.2
4	23	0.5	1.8	<0.3	18.0	21.2	193.7
5	270	409.0	29.2	1422.9	1591.8	2264.3	58475.9
6	157	181.0	81.4	453.4	2739.1	623.4	28713.4
7	-						
8	270	0.3	4.5	25.0	162.4	178.0	675.7

TABLE 5. CALCULATED RELATIVE PERCENTAGE CONTRIBUTION OF CONTAMINANTS FROM PROCESS WASTEWATERS TO TOTAL LOAD INFLUENT TO COMBINED WASTEWATER TREATMENT SYSTEM, i.e. STREAM #5.

Stream ID	Phenol % of total	Sulfide % of total	Ammonia % of total	BOD % of total	TOC % of total	Oil & Grease % of total
1	5.3	390	6.0	59.4	14.0	1.4
2	25.3	1349	19.9	68.0	6.5	0.6
3	35.1	1450	50.9	31.6	14.1	0.2
4	0.1	6	<0.02	1.1	0.9	0.3
6	44.2	279	31.8	172.1	27.5	49.1

contributers of phenol, ammonia, and BOD. The barometric condensor unit appeared to be the most significant source of oil and grease contamination, approximately 50% of total.

Obviously, the calculated relative percent contribution of contaminants from the process wastewater streams was not a precise measure; however, on a relative basis, the calculated percentage contributions provided useful indices for evaluating which process streams were the major contributors to total load of wastewater contaminants.

The concentration of mercury, vanadium, cadmium, and nickel was below detection limits for the atomic absorption spectrometer (Table 6). Detectable quantities of lead were found in process wastewaters from the crude desalting unit and in the combined wastes into the API seperator. The caustic neutralizer process wastewaters appeared to be a major contributor of chromium, zinc, copper, iron, potassium, and sodium. Most of the calcium was found in the crude desalting unit wastewaters, although several other waste streams contributed significant quantities of calcium also.

Analyses of specific organic compounds in the process wastewaters by gas chromatography-mass spectrometry indicated that the waste from the caustic neutralizer and the influent to the API seperator contained the greatest number of compounds which could be identified (Table 7). The most common classes of organic compounds identified in the process waste streams were aliphatic ($C_{10}H_{22}$ to $C_{23}H_{48}$), monocyclic aromatics, and alkyl aromatics. Only 3 polynuclear aromatic hydrocarbons were identified, fluorene, phenanthrene/anthracene, and methyl anthracene. These compounds were found in the caustic neutralizer wastewater. None of the aromatic, alkyl aromatic, or polynuclear aromatic compounds were detected in the final effluent, which would indicate that the biological treatment system at this refinery was effectively removing these compounds. The major class of compounds identified in the final effluent was aliphatic hydrocarbons, a homologous series from $C_{13}H_{28}$ to $C_{20}H_{42}$.

TABLE 6. CONCENTRATION (mg/l) OF HEAVY METALS IN REFINERY A PROCESS WASTEWATER mg/l (ppm)

Sample Identification IPA	Date	Na	Ca	Mg	K	Fe	Pb	Zn	Cu	Cr	Ni	Cd	V	Hg
#1	4-18-80	<1.00	<1.0	<1.0	<1.0	0.19	<0.005	<0.05	<0.05	<0.01	<0.1	<0.005		<0.005
#2	"	15.65	33.99	10.22	4.68	0.79	<0.005	<0.05	<0.05	<0.01	<0.1	<0.005		<0.005
#3	"	12.64	17.26	9.26	2.51	1.21	<0.005	<0.05	<0.05	<0.01	<0.1	<0.005		<0.005
#4	"	785.39	155.51	11.61	15.65	1.66	0.029	<0.05	<0.05	<0.01	<0.1	<0.005		<0.005
#5	"	467.07	106.02	10.81	11.22	2.49	0.029	0.58	<0.05	0.14	<0.1	<0.005		<0.005
#6	"	148.99	26.26	10.23	5.58	1.13	<0.005	0.05	<0.05	0.10	<0.1	<0.005		<0.005
#7	"	4323.23	37.81	11.39	18.57	9.33	<0.005	0.47	0.08	0.14	<0.1	<0.005		<0.005
#8	"	511.67	72.21	11.12	<1.0	0.47	<0.005	0.07	0.05	0.08	<0.1	<0.005		<0.005
EPA Std	EPA / OSU					0.706 / 0.760	0.283 / 0.346	0.48 / 0.44	0.37 / 0.40	0.065 / 0.062	0.165 / 0.160	0.027 / 0.031		0.0076 / 0.0074

#1 - S. Plant to Sour Water Stripper

#2 - N. Plant to Sour Water Stripper

#3 - Water from Sour Water Stripper

#4 - from Desalter

#5 - to API Separator

#6 - from Barometric Condenser

#7 - N. Caustic Neutralizer

#8 - Final Effluent

CLASSES OF ORGANIC COMPOUNDS

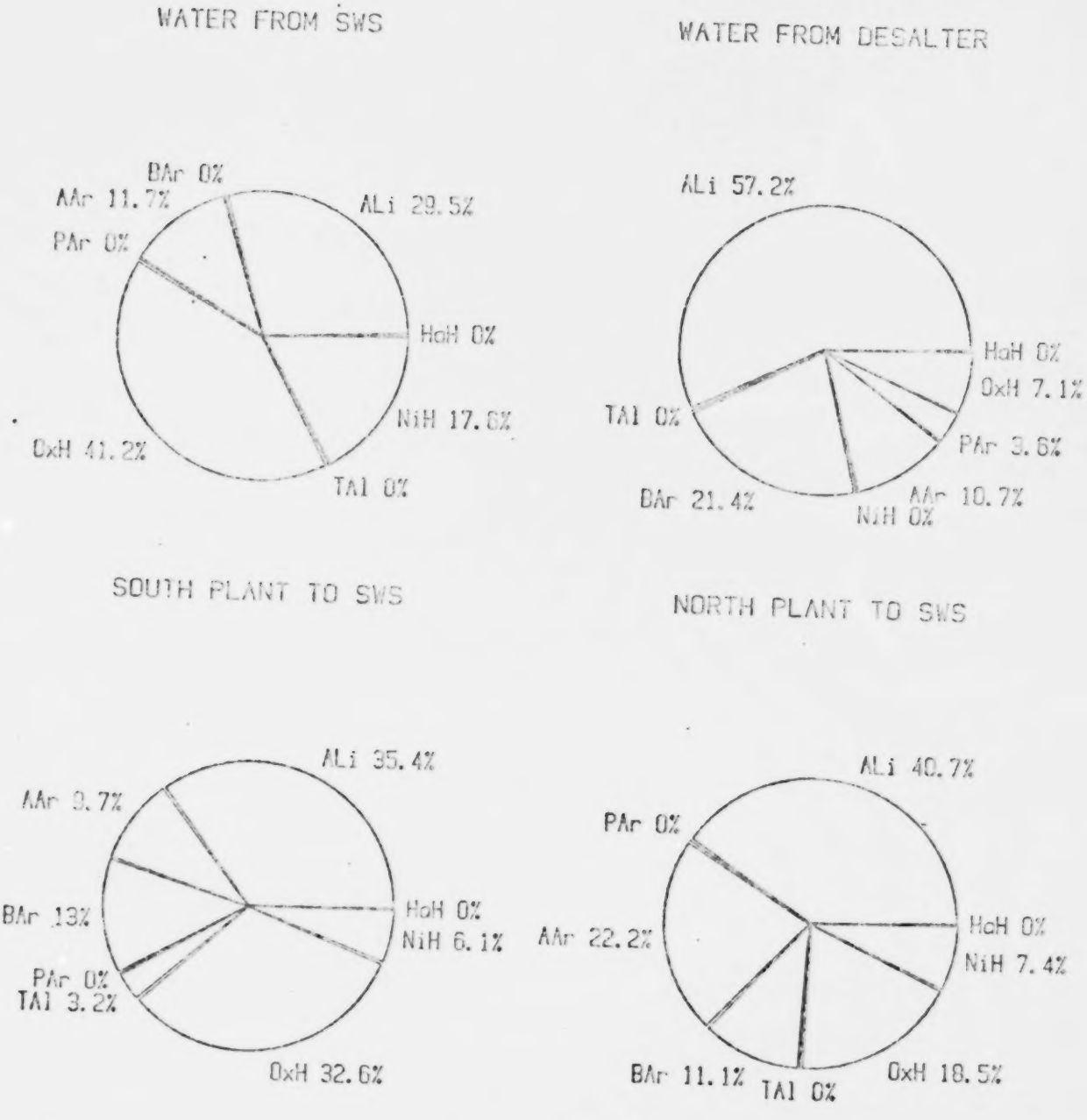
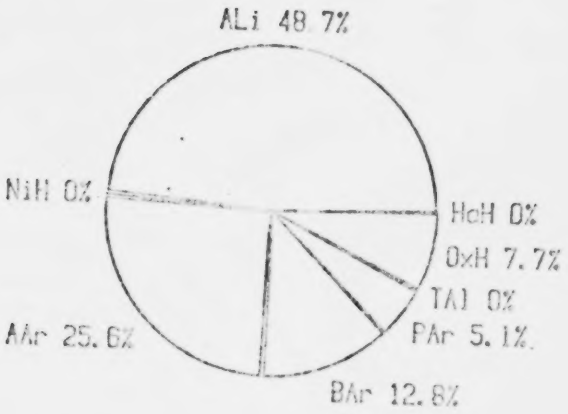


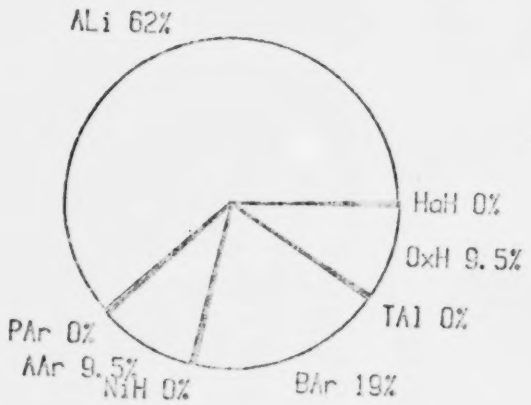
Figure 3. Summary comparison of classes of organic compounds identified in Refinery A process wastewaters.

CLASSES OF ORGANIC COMPOUNDS

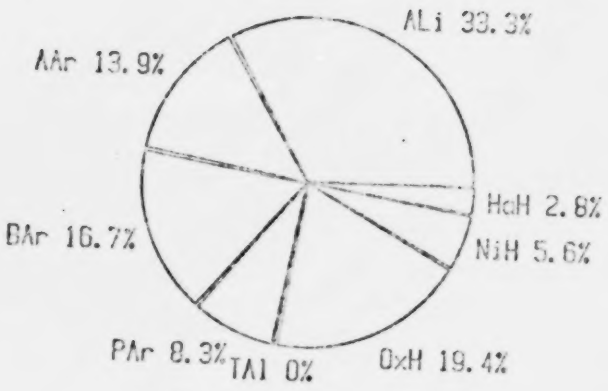
INFLUENT TO API-SEPARATOR



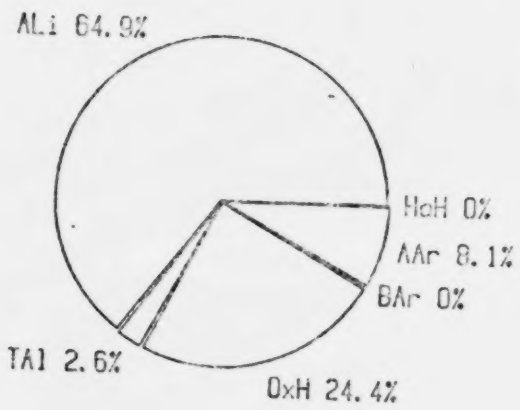
EFFL. FROM BAROMETRIC CONDENSER



N. CAUSTIC NEUTRALIZER



FINAL EFFLUENT



REFINERY .A

Figure 3 (continued)

TABLE 7. SPECIFIC ORGANIC COMPOUNDS IDENTIFIED IN PETROLEUM REFINERY A PROCESS WASTEWATERS BY GAS CHROMATOGRAPHY - MASS SPECTROMETRY

	1*	2*	3*	4*	5*	6*	7*	8*
Dithiobutane							+	
Diacetone-OH							+	
Xylene	+	+	+	+	+	+	+	
Toluene	+	+		+	+	+		
Phenol	+	+	+			+		
$3CH_3$ Hexane		+			+		+	
Isopropyl benzene		+			+		+	
Dichlorobenzene							+	
C_{10} H_{22}	+	+			+	+	+	
$3CH_3$ Benzene					+		+	
C_{11} H_{24}	+	+		+	+	+	+	
Cresol	+	+	+		+	+		
Naphthalene	+	+		+	+	+	+	
C_{12} H_{26}				+	+	+	+	
Quinoline	+						+	

(continued)

TABLE 7 (continued)

	1*	2*	3*	4*	5*	6*	7*	8*
CH_3 Naphthalene	+	+		+	+	+	+	
C_{13} H_{28}	+	+	+	+	+	+	+	+
Biphenyl						+	+	
Ethyl Naphthalene	+			+	+		+	
C_{14} H_{30}	+	+	+	+	+	+	+	+
Dibenzofuran				+			+	
C_3 Naphthalene	+			+	+		+	
Fluorene							+	
C_{15} H_{32}	+	+	+	+	+	+	+	+
C_{16} H_{34}	+	+		+	+	+	+	+
C_{17} H_{36}	+	+		+	+	+	+	
Benzidine							+	
Phenanthrene/Anthracene				+	+		+	
C_{18} H_{38}		+		+	+	+	+	+
C_9 H_{20}	+	+	+		+	+		

(continued)

TABLE 7 (continued)

	1*	2*	3*	4*	5*	6*	7*	8*
C_3 benzene	+	+	+		+			
Indan		+			+			
C_{19} H_{40}		+		+	+		+	+
Cyclohexanone	+						+	
Dimethylpuridine	+							
$3CH_3$ pyridine	+							
C_4 phenol	+	+						
CH_3 Quinoline	+							
Indole	+							
Benzonitrile							+	
Trithiane	+							
bis (2 ethylhexyl) ph	+	+	+	+	+		+	+
Propylbenzene		+			+			
Methylethyl benzene					+			
C_4 benzene		+		+	+		+	

(continued)

TABLE 7 (continued)

	1*	2*	3*	4*	5*	6*	7*	8*
CH_3 isopropbenzene					+		+	+
C_5 benzene					+		+	
$2CH_3$ Dihydroindene					+		+	+
$2CH_3$ naphthalene		+		+	+	+		
C_{20} H_{42}				+	+			
C_{21} H_{44}				+	+			
Pristane	+			+	+	+		
Pyrrole			+					
Pyridine			+					
Aniline		+	+					
$2CH_3$ phenol	+	+	+	+				
$3CH_3$ phenol			+					
C_{22} H_{46}				+	+			
C_{23} H_{48}				+	+			
Phytane	+			+	+	+	+	+
CH_3 Tetrahydro. Naphth.							+	

(continued)

TABLE 7 (continued)

	1*	2*	3*	4*	5*	6*	7*	8*
Di-N-butyl phthalate							+	+
CH_3 Anthracene					+		+	
C_3 Cyclohexane			+			+		
Octylcyclohexane						+		
Toluidine		+	+					
C_3 phenol	+		+					
Ethylphenol								
C_5 Indole								
Ethylhexyl Iodide								
Dimethylethyl Benzene								
Dicyclohexylethare								
Dicyclohexyl propane								
C_4 Naphthalene								

1* - Coker

2* - North Plant to SWS

3* - Sour Water Stripper

4* - Desalter

5* - API Separater

6* - Barometric Condensor

7* - Caustic Neutralizer

8* - Final Effluent

Refinery B

The process wastewater streams sampled at this refinery included the effluent from the SWS, influent to the API separator, and the final effluent from the combined wastewater treatment plant. Due to plumbing configurations and facilities at this refinery, it was not practically feasible to sample the crude desalting unit effluent. We were unable to obtain measurements of flow from the SWS. The refinery personnel provided us with estimated average flow rates of SWS 75 gpm, influent to API separater 550 gpm, and final effluent 700 gpm.

The concentration (mg/l) of phenol, BOD, TOC, and ammonia in the SWS effluent would indicate that it was a major contributor of oxygen consuming contaminants (Table 8). The relative percent contribution of the SWS effluent to total lbs/day of phenol, sulfide, ammonia, and BOD was 17%, 15%, 14%, and 14%, respectively.

TABLE 8. CHARACTERIZATION OF WASTEWATERS FROM PETROLEUM REFINERY B PROCESS UNITS AUGUST 20, 1980

Sample	Phenol mg/l	Sulfide mg/l	Ammonia mg/l	BOD mg/l	TOC mg/l	Oil & Grease mg/l
SWS	158.4	20.8	29.5	425	186	20
API	128.5	10.6	27.5	400	174	442
Weir 3	0.1	0.4	<1.0	30	43	8

The concentration of phenol in the API separator effluent normally ranges from 10 to 20 mg/l (personal communication with refinery personnel). Thus, our composite sample from the influent to the API separator may have been atypical. If the concentration of phenol into the API separator was normally in the 10 to 20 mg/l range, the relative percent contribution of phenol from the FCC unit would be approximately 100% of the total.

No detectable quantities of mercury, vanadium, cadmium, nickel, or copper were found in the wastewaters sampled (Table 9). The SWS effluent showed no significant levels of heavy metals or salts. The influent to the API separator contained relatively high levels of chromium, zinc, and lead, but the concentration was reduced below detectable levels in the final effluent.

The specific organic compounds identified in the base-neutral and weak-acid extracts from Refinery B wastewaters were similar to those

TABLE 9. CONCENTRATION (mg/l) OF HEAVY METALS IN REFINERY B PROCESS WASTEWATER

Sample Identification														
IPA	Date	Na	Ca	Mg	K	Fe	Pb	Zn	Cu	Cr	Ni	Cd	V	Hg
#1	8-21-80	16.76	0.06	<1.0	0.18	0.32	<0.005	<0.05	<0.05	<0.01	<0.1	<0.005		<0.005
#2	"	646.30	86.12	9.92	31.92	0.45	0.005	0.28	<0.05	0.22	<0.1	<0.005		<0.005
#3	"	650.70	107.76	10.48	39.83	0.18	<0.005	<0.05	<0.05	0.02	<0.1	<0.005		<0.005
EPA Std	EPA OSU					0.796 .742	0.383 0.346	.026 .028	.037 .035	.065 .062	.165 .144	0.027 0.031		.0076 .0082

#1 - Sour Water Stripper

#2 - API Trap

#3 - Weir

identified from Refinery A (Table 10). The influent to the API separator contained a homologous series of aliphatic hydrocarbons from $C_{13}H_{28}$ to $C_{30}H_{62}$, monocyclic aromatics, polynuclear aromatics, phenolics, and some organics containing oxygen and nitrogen. The SWS effluent from this refinery did not contain as many mono- or poly- nuclear aromatics as the previous refinery, instead there were more phenolic and partially oxidized organics. The influent to the API separator contained a complex mixture of organics, from which we were able to identify 45 specific compounds. Only nine compounds were identified in extracts from the final effluent. These compounds were mostly phenolic or carboxylic classes.

TABLE 10. PERCENTAGE DISTRIBUTION OF ORGANIC COMPOUNDS IDENTIFIED IN REFINERY B PROCESS WASTEWATERS AMONG SELECTED CLASSES

Class	SWS	API	FINAL EFFL.
Aliphatic	26.6	37.5	0
Alkyl Aromatics	0	3.6	11.1
Bicyclic Aromatics	13.3	8.9	0
Polycyclic Aromatics	0	14.3	0
Thio Alkyls	6.6	3.6	0
Oxygenated Hydrocarbons	53.3	21.4	88.9
Nitrogen Heterocyclics	0	8.9	0
Halogenated Organics	0	1.8	0

TABLE 11. SPECIFIC ORGANIC COMPOUNDS IDENTIFIED IN REFINERY B WASTEWATERS BY GC-MS

	SWS	API	Weir 3
C_9H_{20}			
$C_{10}H_{22}$			
$C_{11}H_{24}$			
$C_{12}H_{26}$			
$C_{13}H_{28}$		+	
$C_{14}H_{30}$		+	
$C_{15}H_{32}$		+	
$C_{16}H_{34}$	+	+	
$C_{17}H_{36}$	+	+	
$C_{18}H_{38}$		+	
$C_{19}H_{40}$	+	+	
$C_{20}H_{42}$		+	
$C_{21}H_{44}$		+	
$C_{22}H_{46}$		+	
$C_{23}H_{48}$		+	
$C_{24}H_{50}$		+	
$C_{25}H_{52}$		+	
$C_{26}H_{54}$		+	
$C_{27}H_{56}$		+	
$C_{28}H_{58}$		+	
$C_{29}H_{60}$		+	

(continued)

TABLE 11 (continued)

	SWS	API	Weir 3
$C_{30}H_{62}$		+	
2,6,10,14-tetramethylpentadecane	+	+	
2,6,10,14-tetramethylpentahexane		+	
methylcyclohexane			
C_3-cyclohexane			
octylcyclohexane			
cyclohexanone			
cyclohexenone			
cyclohexenol			
methylcyclopentenone			
C_3-cyclopentenone			
dicyclohexyl propane			
cicyclohexyl ethane			
toluene			
xylene			
ethylbenzene			
C_3-benzene		+	+
trimethyl benzene			
methylethylbenzene			
n-propylbenzene			
isopropylbenzene			

(continued)

TABLE 11 (continued)

	SWS	API	Weir 3
C_4-benzene		+	
dimethylethylbenzene			
diethylbenzene			
methylisopropylbenzene			
C_5-benzene			
dihydroxydimethylbenzene			
dichlorobenzene			
naphthalene		+	
methylnaphthalene		+	
dimethylnaphthalene	+	+	
ethylnaphthalene	+	+	
C_3-naphthalene		+	
C_4-naphthalene			
C_5-naphthalene			
naphthol			
methyl tetrahydronaphthalene			
biphenyl			
C_2-biphenyl			
acenaphthene			
fluorene		+	
methylfluorene		+	

(continued)

TABLE 11 (continued)

	SWS	API	Weir 3
C_2-fluorene		+	
C_3-fluorene		+	
benzofluorene		+	
anthracene/phenanthrene		+	
methyl(anthracene/phenanthrene)		+	
alkylated(anthracene/phenanthrene)		+	
pyrene/fluoranthene			
phenol	+	+	+
cresol	+	+	+
C_2-phenol			+
dimethylphenol	+	+	
ethylphenol	+	+	+
C_3-phenol		+	
C_4-phenol		+	
C_5-phenol		+	
nitrophenol		+	
aminophenol		+	
chlorophenol		+	
dichlorophenol			
trichlorophenol			
tetrachlorophenol			

(continued)

TABLE 11 (continued)

	SWS	API	Weir 3
bromophenol			
toluidine			
aniline	+		
benzidine			
dibenzofuran			
pyrrole			
pyridine			
dimethylpyridine			
C_3-pyridine			
benzonitrile			
indole			
methyl indole		+	
Indan			
methyldihydroindene		+	
dimethyldihydroindene	+	+	
quinoline			
methyl quinoline		+	
dimethyl quinoline		+	
nitrosomorphosoline		+	
dimethylnitrosoamine		+	
trithiane			

(continued)

TABLE 11 (continued)

	SWS	API	Weir 3
dithiabutane			
dibenzothiophene			
methyl benzothiophene			
methyl dibenzothiophene			
methylthiacyclopentane			
acetic acid			
butyric acid	+		
carboxylic acids	+	+	+
methylcarboxylic acids	+		+
methyl benzoic acid			
diethyl phthalate		+	
di-n-butylphthalate			+
bis(2-ethylhexyl)phthalate	+	+	+
hydroxymethyldimethylhydantoin			
diacetone alcohol			
ethylhexyliodide			

Refinery C

Samples were manually collected from Refinery C on 9 October 1980. Previous plans to collect samples at 6 h intervals for compositing had to be cancelled due to some unforeseen problems encountered by Refinery C personnel in operation of the process units. These conditions around the process units where we needed to sample made it necessary to limit time of access to short intervals accompanied by an experienced refinery process operator. We elected to collect a single "grab" sample from each process unit rather than delay the sampling process until conditions improved.

Samples were collected from East Plant SWS effluent, South Plant SWS effluent, influent to Thermal Division API separator, and influent to Light Oil Division API separator. The stripped bottoms from both of the SWS units contained high concentrations of phenol, BOD, and TOC (Table 12). High concentrations of these parameters indicate that these process streams contribute a significant proportion of the total oxygen consuming contaminants to the combined wastewater treatment system. The concentration of sulfides and ammonia ranged from 30.6 to 38.4 and 14 to 22 mg/l respectively.

The concentration of mercury and nickel was below detectable levels in all the process streams sampled (Table 13). Detectable concentrations of vanadium, cadmium, chromium, copper, zinc, and lead were found in the influent to the TCD-API unit. This process waste stream also contained significantly higher concentrations of iron and chromium than the other streams.

The specific organic compounds identified with GC-MS in solvent extracts from Refinery C process wastewaters were very similar to compounds previously identified at the other refineries surveyed (Table 15). The classes of compounds identified included aliphatics, aromatics, polynuclear aromatics, and compounds containing oxygen and nitrogen (Tables 14 and 15).

TABLE 12. CONCENTRATION OF MAJOR CONTAMINANTS IN REFINERY C PROCESS WASTEWATERS, OCTOBER 9, 1980

	Phenol mg/l	Sulfide mg/l	Ammonia mg/l	BOD mg/l	TOC mg/l	Oil and Grease mg/l
SWS-East Plant	432.4	38.4	14	2700	626	44.5
SWS-South Plant	224.7	30.6	22	3200	635	228.3
TCD-API	20.0	7.5	444	>2000	90	3088.
Light Oil-API	10.8	7.9	400	>1900	134	772.

TABLE 13. CONCENTRATION (mg/l) OF HEAVY METALS IN REFINERY C PROCESS WASTEWATERS, OCTOBER 9, 1980

SAMPLE IDENTIFICATION	DATE	Na	Ca	Mg	K	Fe	Pb	Zn
1. Lt. Oil API	10-9-80	24.72	84.41	19.20	26.71	0.80	0.115	0.14
2. SWS E. Plant	"	<1.00	<1.00	<1.00	<0.50	1.93	<0.005	0.25
3. TCD API effl.	"	28.25	50.38	22.35	27.98	15.36	0.022	0.46
4. SWS S. Plant	"	22.13	<1.00	<1.00	<0.50	1.54	0.005	0.05
	EPA					0.078	0.113	0.478
	OSU					0.078	0.101	0.433

SAMPLE IDENTIFICATION	DATE	Cu	Cr	Ni	Cd	V	Hg
1. Lt. Oil API	10-9-80	<0.05	0.151	<0.1	<0.005	<0.005	<0.005
2. SWS E. Plant	"	0.91	0.024	<0.1	<0.005	<0.005	<0.005
3. TCD API effl.	"	0.05	0.336	<0.1	0.008	0.060	<0.005
4. SWS S. Plant	"	0.05	0.032	<0.1	0.048	<0.005	<0.005
	EPA	0.037	0.065	0.096	0.027	0.004	0.0076
	OSU	0.038	0.064	0.109	0.030	0.003	0.0109

TABLE 14. PERCENTAGE DISTRIBUTION OF ORGANIC COMPOUNDS IDENTIFIED IN REFINERY C PROCESS WASTEWATERS AMONG SELECTED CLASSES

Class	SWS-East	SWS-South	TCD-API	Lt. Oil-API
Aliphatic	23.1	47.8	20.4	25.0
Alkyl Aromatics	7.7	4.3	29.5	12.5
Bicyclic Aromatics	0	0	9.1	12.5
Polycyclic Aromatics	0	0	6.8	10.0
Thio Alkyls	7.7	0	6.8	2.5
Oxygenated Hydrocarbons	46.1	26.0	15.9	22.5
Nitrogen Heterocyclics	15.4	21.7	6.8	7.5
Halogenated Hydrocarbons	0	0	4.5	7.5

TABLE 15. SPECIFIC ORGANIC COMPOUNDS IDENTIFIED BY GC-MS IN EXTRACTS FROM REFINERY C PROCESS WASTEWATERS

	SWS EAST	SWS SOUTH	TCD API	LIGHT OIL API
C_9H_{20}	+			
$C_{10}H_{22}$	+	+		
$C_{11}H_{24}$		+	+	
$C_{12}H_{26}$		+	+	
$C_{13}H_{28}$	+	+	+	+
$C_{14}H_{30}$		+	+	+
$C_{15}H_{32}$		+	+	+
$C_{16}H_{34}$		+	+	+
$C_{17}H_{36}$		+	+	+
$C_{18}H_{38}$		+	+	+
$C_{19}H_{40}$				+
$C_{20}H_{42}$				
$C_{21}H_{44}$				
$C_{22}H_{46}$				
$C_{23}H_{48}$				
$C_{24}H_{50}$				
$C_{25}H_{52}$				
$C_{26}H_{54}$				
$C_{27}H_{56}$				
$C_{28}H_{58}$				
$C_{29}H_{60}$				

(continued)

TABLE 15 (continued)

	SWS EAST	SWS SOUTH	TCD API	LIGHT OIL API
$C_{30}H_{62}$				
2,6,10,14-tetramethylpentadecane		+		+
2,6,10,14-tetramethylpentahexane		+		+
methylcyclohexane				
C_3-cyclohexane				
octylcyclohexane				
cyclohexanone				
cyclohexenone				
cyclohexenol				
methylcyclopentenone				
C_3-cyclopentenone				
dicyclohexyl propane				
dicyclohexyl ethane				
toluene			+	
xylene			+	+
ethylbenzene			+	
C_3-benzene	+	+	+	
trimethyl benzene			+	+
methylethylbenzene			+	
n-propylbenzene			+	
isopropylbenzene			+	

(continued)

TABLE 15 (continued)

	SWS EAST	SWS SOUTH	TCD API	LIGHT OIL API
C_4-benzene			+	+
dimethylethylbenzene			+	
diethylbenzene			+	
methylisopropylbenzene				
C_5-benzene				
dihydroxydimethylbenzene				
dichlorobenzene				
naphthalene			+	+
methylnaphthalene			+	+
dimethylnaphthalene			+	+
ethylnaphthalene			+	
C_3-naphthalene				+
C_4-naphthalene				
C_5-naphthalene				
naphthol			+	+
methyl tetrahydronaphthalene				
biphenyl				+
C_2-biphenyl				
acenaphthene			+	+
fluorene				+
methylfluorene				

(continued)

TABLE 15 (continued)

	SWS EAST	SWS SOUTH	TCD API	LIGHT OIL API
C_2-fluorene				
C_3-fluorene				
benzofluorene				
anthracene/phenanthrene			+	+
methyl(anthracene/phenanthrene)			+	+
alkylateo(anthracene/phenanthrene)				+
pyrene/fluoranthene				
phenol	+	+		+
cresol	+	+	+	+
C_2-phenol				
dimethylphenol	+	+	+	
ethylphenol	+	+		+
C_3-phenol	+	+	+	+
C_4-phenol			+	+
C_5-phenol			+	+
nitrophenol				
aminophenol				
chlorophenol				
dichlorophenol				+
trichlorophenol				+
tetrachlorophenol				+

(continued)

TABLE 15 (continued)

	SWS EAST	SWS SOUTH	TCD API	LIGHT OIL API
bromophenol			+	
toluidine				
aniline	+	+	+	
benzidine				
dibenzofuran				
pyrrole				
pyridine				
dimethylpyridine				
C_3-pyridine				
benzonitrile				
indole	+	+	+	+
methyl indole			+	+
Indan			+	+
methyldihydroindene			+	+
dimethyldihydroindene				
quinoline				
methyl quinoline				
dimethyl quinoline			+	
nitrosomorphosoline				
dimethylnitrosoamine				
trithiane				

(continued)

TABLE 15 (continued)

	SWS EAST	SWS SOUTH	TCD API	LIGHT OIL API
dithiabutane			+	
dibenzothiophene	+		+	+
methyl benzothioplene				
methyl dibenzothiophene				
methylthiacyclopentane			+	
acetic acid		+		
butyric acid				
carboxylic acids		+		+
methylcarboxylic acids				
methyl benzoic acid		+		
diethyl phthalate				+
di-n-butylphthalate				
bis(2-ethylhexyl)phthalate	+	+	+	+
hydroxymethyldimethyldydantoin				
diacetone alcohol				
ethylhexyliodide				

PHASE 2. COMPARISON OF PILOT SCALE MIXED MEDIA FILTER-ACTIVATED CARBON VERSUS BIOPOND TREATMENT OF SOURWATER STRIPPER PROCESS WASTEWATER

First 30-Day On-Site Evaluation

The calculated mean percentage removal of phenol by the biopond was 99.87% and for the MMF-AC pilot scale treatment unit 99.99% (Table 16). The mean concentration of phenol in the effluent from the SWS unit was 203 mg/l with a range from 175 to 233 mg/l in the first on-site evaluation (Table 17). The mean concentration of phenol in the effluent from the biopond system was 0.269 mg/l with a range from 0.031 to 0.449 mg/l. The mean concentration of phenol in the effluent from the MMF-AC pilot scale treatment system was 0.002 mg/l with a range from <0.001 to 0.004 mg/l.

TABLE 16. CALCULATED MEAN PERCENT REMOVAL OF CONTAMINANTS FROM THE SWS PROCESS WASTEWATERS BY THE FULL SCALE BIOPOND AND THE PILOT SCALE MMF-AC UNITS

	Phenol	Sulfide	Ammonia	BOD	TOC	Oil & Grease
Biopond	99.87%	100%	24.8%	90.1%	90.9%	95.5%
MMF-AC	99.99%	100%	11.6%	95.3%	96.9%	99.8%

The mean percentage removal of phenol, BOD, TOC, and Oil & Grease by the MMF-AC pilot scale unit was greater than the biopond unit. The biopond unit was more effective at reducing the concentration of ammonia.

The mean concentration of cations in the first 30 day run indicates there was some removal of divalent cations on the MMF-AC units, especially calcium, magnesium, iron, copper, and chromium (Table 18). The concentration of sodium and potassium was not affected. The mean concentration of selenium actually increased slightly. The concentration of nickel, arsenic, vanadium, and mercury was generally below detection limit (Appendix A, Tables A1 to A5).

TABLE 17. CHEMICAL ANALYSES OF SOURWATER STRIPPER PROCESS EFFLUENT AND COMPARISON OF TWO TYPES OF TREATMENT SYSTEMS, BIOPOND AND ACTIVATED CARBON, AT REFINERY DPQ.

PROCESS STREAM	DATE	PHENOL	SULFIDE	AMMONIA	BOD	TOC	OIL & GREASE
Sourwater Stripper	9-14-81	204.9	16.6	89.2	340	425	37
" "	9-22-81	175.8	12.8	80.0	860	451	169
" "	9-28-81	207.6	10.3	93.9	900	476	368
" "	10-5-81	233.7	11.1	91.8	484	343	1,690
" "	10-8-81	194.9	19.9	84.0	3,850	7,579	10,380
		$\bar{x}$ 203	$\bar{x}$ 14.1	$\bar{x}$ 87.8	$\bar{x}$ 1,287	$\bar{x}$ 1,855	$\bar{x}$ 2,529
Biopond Effluent	9-14-81	0.031	<3.0	56.8	75	100	<5
" "	9-22-81	0.208	<3.0	56.0	68	127	20
" "	9-28-81	0.449	<3.0	77.4	245	291	414
" "	10-5-81	0.304	<3.0	34.4	67	161	64
" "	10-8-81	0.351	<3.0	51.9	178	164	66
		$\bar{x}$ 0.269	$\bar{x}$ <3.0	$\bar{x}$ 55.3	$\bar{x}$ 127	$\bar{x}$ 169	$\bar{x}$ 113
Activated Carbon	9-14-81	0.004	<3.0	<1.0	2	4	<5
" "	9-22-81	0.001	<3.0	90.0	49	35	7
" "	9-28-81	<0.001	<3.0	175.4	61	81	<5
" "	10-5-81	0.003	<3.0	40.6	42	60	<5
" "	10-8-81	<0.001	<3.0	82.0	150	103	<5
		$\bar{x}$ 0.002	$\bar{x}$ <3.0	$\bar{x}$ 77.6	$\bar{x}$ 61	$\bar{x}$ 57	$\bar{x}$ <5

TABLE 18. MEAN CONCENTRATION (mg/l) OF SELECTED CATIONS IN REFINERY C WASTEWATERS DURING THE FIRST ON-SITE EVALUATION 9/14 to 10/8, 1981

	Na	Ca	Mg	K	Fe	Zn	Cu	Cr	Se
SWS	44.4	20.0	4.3	1.7	0.36	0.06	0.01	0.04	0.07
Biopond	158.4	53.9	7.9	5.3	0.35	0.03	0.01	0.04	0.24
MMF-AC	49.6	8.5	2.6	2.2	0.12	0.03	<0.05	<0.01	0.19

Prior to breakthrough, the mean concentration of BOD and TOC from the MMF-AC unit was 38.5 mg/l and 45.0 mg/l, respectively. Breakthrough of BOD and TOC occurred between 10/5/81 and 10/8/81 when BOD increased from 42 to 150 mg/l and TOC increased from 60 to 103 mg/l. Overall, the effectiveness of the biopond system would appear to be equivalent or superior to that of the mixed media-activated carbon treatment system. This conclusion was based upon the difficulty in predicting "breakthrough" point for the activated carbon units.

The biopond system with the large stabilization basin appeared to be capable of absorbing "shock" loads of high concentrations of organics without malfunction of the biodegradation capacity. Therefore, this system, while not capable of achieving the same overall reductions as the MMF-AC during initial stages of the test, would appear to be more reliable for handling the large fluctuations in concentration of waste organics. In addition, the biopond required minimal supervision by refinery personnel.

Organic Analysis of Sour Water Stripper Effluent

The sour water stripper effluent was a complex mixture of organic compounds. The base-neutral fraction was passed through a silica gel cleanup which produced hexane, benzene, and methanol fractions.

The methanol fraction was a complex mixture of polar compounds which could not be adequately separated for the generation of clean mass spectra. Quantitation of the methanol fractions was not possible for most of the samples.

A total of 75 to 80 compounds were identified in the hexane and benzene fractions. The hexane fraction contained mostly aliphatic compounds while the benzene fraction consisted chiefly of aromatics. Some compounds were present in both fractions. About 30 parent compounds were identified in the two fractions (Tables 19-22). Many alkylated parent compounds were also present in the fractions. Ten of the organic compounds are on the EPA priority pollutant list.

The acid fraction consisted mainly of phenolic compounds, although some base-neutral compounds occasionally occurred in that fraction. The acid fraction was not quantified, since phenolic analysis was run on each sample.

Organic Analysis of Carbon Effluent

The carbon effluent was fairly clean until 9-28-81. Breakthrough began on 9-28-81 and increased by 10-5-81. Many compounds present in the carbon effluent could not be identified, and therefore are not priority pollutants or other common pollutants. The compounds identified were low molecular weight acids and bases, which would be relative soluble in water (Tables 19-22). Those compounds were not normally identified in the sour water stripper effluent. They may be products of biological or chemical reactions of other organics adsorbed on the carbon.

Organic Analysis of Biopond Effluent

The Biopond effluent was a consistently complex mixture of mostly unidentified organics. The compounds which were identified were predominantly nitrogen and oxygen containing organics (Tables 19-22). The apparent polarity of the compounds in the biopond waste and the absence of their spectra from the data bases indicate that many of those compounds may be bacterial metabolic products. No priority pollutants were found in the biopond effluent on a consistent basis.

The biopond appears to be an effective treatment for the removal of the priority pollutants identified in the sour water stripper effluent. It consistently reduced the organics load as measured by the TOC, BOD, oil and grease, and gas chromatographic analyses.

The activated carbon system removed priority pollutants and most other organic compounds. Oil and grease values were low for the entire first run. BOD and COD valves were low at the beginning of the run and increased until

the end of the run. Flow during the first 30 day evaluation was not continuous. During the second 30 day evaluation the flow was continuous except for a short period. BOD, TOC, and oil and grease were low at the start of the second 30 day evaluation and increased rapidly to values much higher than the biopond.

TABLE 19. LIST AND CONCENTRATION (ug/l) OF SPECIFIC ORGANIC COMPOUNDS ISOLATED FROM REFINERY C WASTEWATERS, 9-14-81

Compound	# ISO	MMF-AC BNC	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Toluene								+			
Naphthalene											
Methyl Naphthalene											
Dimethyl Naphthalene											
Ethyl Naphthalene											
C_3 Naphthalene	3					+					
C_4 Naphthalene											
Biphenyl											
Methyl Biphenyl											
Ethyl Biphenyl											
C_3 Biphenyl											
Diphenylethylene											
Anthracene/Phenan.											
Methyl (A/P)	2						3				
Ethyl (A/P)											
Dimethyl (A/P)											
C_3 (A/P)											

(continued)

TABLE 19 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Pyrene/fluoranthene							+				
Phenol		29					3926		+		
Cresol	3						5532	+	+		
Dimethylphenol							+		+		
Ethylphenol							672				
C_3 phenol							23				
Fluorene											
Methyl Fluorene											
C_2 Fluorene											
Indole							61				
Methyl Indole	3						33	+			
C_2-Indole											
Dibenzothiophene											
Methyl Dibenzothiophene											
Methyl Dihydroindene											
Dimethyl Dihydroindene											
Benzoic Acid											
Ethyl Isothiocyanate											
Cyclohexylamine											

(continued)

TABLE 19 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Butoxyethanol											
Aniline								+			
Toluidine											
Nitrosocarbazole											
Dibenzofuran											
Benzofluorene											
C_{12}											
C_{13}											
C_{14}											
C_{15}											
C_{16}											
Pristane											
C_{17}											
C_{18}						+					
Phytane											
C_{19}						+					
C_{20}						+					
C_{21}						+					
C_{22}						+					

(continued)

TABLE 19 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
C_{23}						+					
C_{24}						+					
C_{25}						+					
Methyl Carbazole	4						235	+			
C_2 Carbazole	3						123	+			
C_3 Carbazole											
Acetic Acid											
Butyric Acid											
Valeric Acid											
Chrysene											
Carbazole							142	+			
Diethyl Phthalate		64	32								
Trichloropropene		+									
Quinoline							+				
Benzamide							+				
Butyric Acid						+			+		
Styrene						+					
C_2 Piperidine						+					

(continued)

TABLE 19 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
C_3 Piperidine					+						
Methyl Sulfinyl Benzene					+						
Di-n-butyl Phthalate					+						

Legend

+ = identified but not sufficient quantity to accurately quantify

ISO = number of isomers identified

MMF-AC = pilot scale mixed media filter-activated carbon unit

BP = full scale biopond treatment unit

SWS = sourwater stripper process unit

BN = base neutral extract

ACID = acid extract

HEX = hexane elution fraction from silica gel column clean-up of base neutral extract

BENZ = benzene elution fraction from silica gel column clean-up of base neutral extract

METH = methanol elution fraction from silica gel column clean-up of base neutral extract

VOL = volatile organics by nitrogen purge and trap on TENAX GC adsorbent, thermal desorbtion onto GC column

TTL = Total concentration of compound found in all fractions or extracts

TABLE 20. LIST AND CONCENTRATION (ug/l) OF SPECIFIC ORGANIC COMPOUNDS ISOLATED FROM REFINERY C WASTEWATERS, 9-22-81

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Toluene										+	
Naphthalene						+					
Methyl Naphthalene	2					228	23				251
Dimethyl Naphthalene	3					484	263		774		1521
Ethyl Naphthalene							48		69		117
C_3 Naphthalene	5					511	264		567		1342
C_4 Naphthalene	2					+	23		+		23
Biphenyl							5				5
Methyl Biphenyl	2						94				94
Ethyl Biphenyl						+	24				24
C_3 Biphenyl									+		
Diphenylethylene							+				
Anthracene/Phenan.							213		467		680
Methyl (A/P)	3						236		11		247
Ethyl (A/P)							54				54
Dimethyl (A/P)							51		+		51
C_3 (A/P)									+		

(continued)

TABLE 20 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Pyrene/fluoranthene									217		217
Phenol		18							152195		152195
Cresol		6					357		43838		44195
Dimethylphenol	2						156				156
Ethylphenol							84				84
C_3 phenol									+		
Fluorene									+		
Methyl Fluorene						+					
C_2 Fluorene											
Indole							230				230
Methyl Indole	3						178				178
C_2-Indole							25				25
Dibenzothiophene									+		
Methyl Dibenzothiophene							+		+		
Methyl Dihydroindene						+					
Dimethyl Dihydroindene						+					
Benzoic Acid									+		
Ethyl Isothiocyanate										+	
Cyclohexylamine						NQ					

(continued)

TABLE 20 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Butoxyethanol						NQ					
Aniline						NQ					
Toluidine						+					
Nitrosocarbazole							137				137
Dibenzofuran							+				
Benzofluorene						+					
C_{12}						14					14
C_{13}											
C_{14}						218					218
C_{15}						221					221
C_{16}						516		292			808
Pristane						80		202			282
C_{17}						390		493			883
C_{18}						267		395			662
Phytane						÷		+			
C_{19}						225		552			777
C_{20}						126		254			380
C_{21}						61		160			221
C_{22}						+		85			85

(continued)

TABLE 20 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
C_{23}						+			+		
C_{24}						+			+		
C_{25}						+			+		
Methyl Carbazole						+			+		
C_2 Carbazole											
C_3 Carbazole											
Acetic Acid											
Butyric Acid											
Valeric Acid											
Chrysene											
Acenaphthene						31					31
Carbazole						+					
C_2 Piperidine					NQ						
C_3 Piperidine					NQ						

TABLE 21. LIST AND CONCENTRATION (ug/l) OF SPECIFIC ORGANIC COMPOUNDS ISOLATED FROM REFINERY C WASTEWATERS, 9-28-81

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Toluene											
Naphthalene											
Methyl Naphthalene	2					67	19				86
Dimethyl Naphthalene	6					224	98		NQ		
Ethyl Naphthalene						32	5				
C_3 Naphthalene	7					78	66		NQ		
C_4 Naphthalene	2					+	8				
Biphenyl											
Methyl Biphenyl									NQ		
Ethyl Biphenyl											
C_3 Biphenyl											
Diphenylethylene											
Anthracene/Phenan.						13	103		NQ		
Methyl (A/P)	6					+	136		NQ		
Ethyl (A/P)											
Dimethyl (A/P)	4						39		NQ		
C_3 (A/P)	2						7				

(continued)

TABLE 21 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Pyrene/fluoranthene											
Phenol						+	+		NQ		
Cresol						+	+	NQ	NQ		
Dimethylphenol											
Ethylphenol								NQ			
C_3 phenol											
Fluorene							22				
Methyl Fluorene	3						37				
C_2 Fluorene											
Indole								NQ			
Methyl Indole								NQ			
C_2-Indole											
Dibenzothiophene							40				
Methyl Dibenzothiophene	2						40				
Methyl Dihydroindene											
Dimethyl Dihydroindene											
Benzoic Acid											
Ethyl Isothiocyanate											
Cyclohexylamine											

(continued)

TABLE 21 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Butoxyethanol											
Aniline								NQ			
Toluidine								NQ			
Nitrosocarbazole											
Dibenzofuran											
Benzofluorene											
C_{12}											
C_{13}									NQ		
C_{14}				NQ					NQ		
C_{15}				NQ	NQ				NQ		
C_{16}				NQ	NQ	75			NQ		
Pristane				NQ	NQ	28					
C_{17}				NQ	NQ	65			NQ		
C_{18}				NQ	NQ	75			NQ		
Phytane				NQ	NQ	6			NQ		
C_{19}				NQ	NQ	58			NQ		
C_{20}				NQ	NQ	80			NQ		
C_{21}				NQ	NQ	73			NQ		
C_{22}				NQ	NQ	33			NQ		

(continued)

TABLE 21 (continued)

Compound	# ISO	MMF-AC BM	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
C_{23}					NQ	17			NQ		
C_{24}					NQ	+					
C_{25}											
Methyl Carbazole	5							NQ			
C_2 Carbazole	4							NQ			
C_3 Carbazole	4							NQ			
Acetic Acid											
Butyric Acid											
Valeric Acid											
Chrysene											
C_2 Piperidine	2				NQ						
C_3 Piperidine	2				NQ						
Acenaphthene						4	10				
Cyacenaphthene						+					
Methyl Acenaphthene						+	17				
Carbazole							10	NQ			
Methyl Pyrrolidinone					NQ						
C_2 Pyrrolidinone					NQ						

(continued)

TABLE 21 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
C_{23}			NQ	NQ							
C_{24}			NQ								
C_{25}			NQ								
Methyl Carbazole			NQ								

TABLE 22. LIST AND CONCENTRATION (ug/l) OF SPECIFIC ORGANIC COMPOUNDS ISOLATED FROM REFINERY C WASTEWATERS, 10-8-81

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Toluene			NQ				+				
Naphthalene						+					
Methyl Naphthalene	2					2200	712				
Dimethyl Naphthalene	10					25514	4352				
Ethyl Naphthalene						+	223				
C_3 Naphthalene	16					29960	2691				
C_4 Naphthalene	13					7898	878				
Biphenyl							+				
Methyl Biphenyl	4					2654	1486				
C_2 Biphenyl					+	4090	572				
C_3 Biphenyl											
Diphenylethylene											
Anthracene/Phenan.						4670	8300				
Methyl (A/P)	4					4586	15920				
C_2 (A/P)											
Dimethyl (A/P)	8					9307	7620				
C_3 (A/P)	2					1655	+				

(continued)

TABLE 22 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Pyrene/fluoranthene						777	+				
Phenol											
Cresol											
Dimethylphenol											
Ethylphenol											
C_3 phenol											
Fluorene						10899	1431				
Methyl Fluorene						+					
C_2 Fluorene						+					
Indole											
Methyl Indole											
C_2-Indole											
Dibenzothiophene							994				
Methyl Dibenzothiophene	2					+	681				
Methyl Dihydroindene											
Dimethyl Dihydroindene						36					
Benzoic Acid											
Ethyl Isothiocyanate											
Cyclohexylamine											

(continued)

TABLE 22 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Butoxyethanol											
Aniline											
Toluidine											
Nitrosocarbazole											
Dibenzofuran							512				
Benzofluorene							+				
C_{12}						1838	+				
C_{13}						6363	212				
C_{14}						6799	375				
C_{15}					NQ	10243	1106				
C_{16}					NQ	14852	906				
Pristane					NQ	3003					
C_{17}					NQ	16070	1988				
C_{18}				NQ	NQ	12736	694				
Phytane				NQ	NQ	3071					
C_{19}				NQ	NQ	13366	138				
C_{20}				NQ	NQ	6825					
C_{21}				NQ	NQ	3885					
C_{22}				NQ	NQ	2116					

(continued)

TABLE 22 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
C_{23}					NQ	945					
C_{24}					NQ	410					
C_{25}											
Methyl Carbazole											
C_2 Carbazole											
C_3 Carbazole											
Acetic Acid											
Butyric Acid											
Valeric Acid											
Chrysene											
Methyl Dibenzofuran							1088				
C11						746	+				
Acenaphthene							+				
C_2 Dibenzothiophene						+	+				
Chrysene/benzo(a) anthracene											
Cyclohexenone					NQ						
C_2Piperidine					NQ						
C_3 Piperidine					NQ						

(continued)

TABLE 22 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
C10						252					
C_3 Dihydroindene	2					532					
C_4 Dihydroindene						208					
Isobutylamide			+								

Second 30-Day On-Site Evaluation

The mean percent removal of phenol and sulfides by the biopond from the SWS waste stream was greater than 99% (Table 23). The MMF-AC unit performed at nearly 100% removal of phenol, BOD and oil and grease for the first 2 days of operation; however, breakthrough began to occur on the second day as indicated by increase in BOD and TOC (Table 24). By the seventh day of operation, the concentration of oil and grease increased significantly, indicating breakthrough of nonpolar organic contaminants. Although the carbon continued to adsorb some of the influent organics throughout the remainder of the test, there was significant leaching of organics from the carbon.

Neither the biopond nor the MMF-AC units affected concentration of major cations significantly (Table 25). In most cases the concentration of sadium, calcium, magnesium, and potassium in the effluent from the treatment units was greater than from the SWS process wastewater. This was understandable for the biopond, since it received additional process wastewaters from coking unit and some others unknown to us. However, the increase from the MMF-AC unit was unexpected. Some of the increase must have leached from the activated carbon.

The list of specific organic compounds and concentration (ug/l) identified in Refinery C wastewaters during the second on-site evaluation indicated a progressive increase in non-polar organic compounds, i.e. aliphatics and aromatics, as the adsorption capacity of the activated carbon was exceeded (Tables 26-30).

TABLE 23. CALCULATED MEAN PERCENT REMOVAL OF CONTAMINANTS FROM THE SWS PROCESS WASTEWATERS BY THE FULL SCALE BIOPOND AND THE PILOT SCALE MMF-AC UNITS.

	Phenol	Sulfide	Ammonia	BOD	TOC	Oil & Grease
Biopond	99.9	100.0	46.9	87.2	71.7	90.0
MMF-AC	64.9	100.0	22.9	60.0	60.0	98.1

TABLE 24. CONCENTRATION (mg/l) OF CONVENTIONAL CONTAMINANTS IN REFINERY C WASTEWATERS DURING SECOND ON-SITE EVALUATION

PROCESS STREAM	DATE	PHENOL	SULFIDE	AMMONIA	BOD	TOC	OIL & GREASE
Sourwater Stripper	10-26-81	200.12	16	96	722	372	1335
" "	10-28-81	168.18	11	98	724	440	584
" "	10- 2-81	214.96	12	92	1262	837	291
" "	11- 9-81	182.96	11	65	706	603	168
" "	11-16-81	187.20	13	63	970	558	--
		$\bar{x}$ 190.68	$\bar{x}$ 13	$\bar{x}$ 83	$\bar{x}$ 877	$\bar{x}$ 562	$\bar{x}$ 595
Biopond Effluent	10-26-81	0.414	<3	44	136	218	67
" "	10-28-81	0.225	<3	59	107	208	90
" "	11- 2-81	0.110	<3	54	121	126	11
" "	11- 9-81	0.128	<3	35	128	161	73
" "	11-16-81	0.232	<3	30	68	84	--
		$\bar{x}$ 0.222	$\bar{x}$ <3	$\bar{x}$ 44	$\bar{x}$ 112	$\bar{x}$ 159	$\bar{x}$ 60
Activated Carbon	10-26-81	<.025	<3	47	3	13	<5
" "	10-28-81	0.014	<3	75		184	<5
" "	11- 2-81	<.025	<3	80	375	287	12
" "	11- 9-81	126.56	<3	63	474	284	32
" "	11-16-81	207.70	<3	58	552	356	13
		$\bar{x}$ 66.85	$\bar{x}$ <3	$\bar{x}$ 64	$\bar{x}$	$\bar{x}$ 225	$\bar{x}$ 11

TABLE 25. MEAN CONCENTRATION (mg/l) OF CATIONS IN REFINERY C WASTEWATERS DURING SECOND ON-SITE EVALUATION, 10/26 - 11/16, 1980

Stream	Na	Ca	Mg	K	Fe	Zn	Cu	Cr	Se
SWS	22.4	6.0	1.0	0.7	0.15	0.01	0.05	0.02	0.76
Biopond	125.0	24.6	5.0	3.5	0.13	<0.05	<0.05	0.01	0.36
MMF-AC	39.0	27.6	16.4	1.8	<0.10	<0.05	<0.05	<0.01	0.56

TABLE 26. LIST AND CONCENTRATION (ug/l) OF SPECIFIC ORGANIC COMPOUNDS ISOLATED FROM REFINERY C WASTEWATERS, 10-26-81

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Toluene											
Naphthalene						7	+				
Methyl Naphthalene	2					123	53				
Dimethyl Naphthalene	5					300	93				
Ethyl Naphthalene	3					35	33				
C_3 Naphthalene	9					34	75				
C_4 Naphthalene	4					68	5				
Biphenyl						21	3				
Methyl Acenaphthene/ Biphenyl	4					54	68				
C_2 Acenaphthene/Biphenyl	5				+	+	84				
C_3 Acenaphthene/Biphenyl											
Diphenylethylene											
Anthracene/Phenanthrene							95				
Methyl (A/P)	4					24	127				
C_2 (A/P)	2					15	21				
C_3 (A/P)											

(continued)

TABLE 26 (continued)

Compound	# ISO	MMF-AC BN	MMC-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Pyrene/fluoranthene						+					
Phenol											
Cresol											
Dimethylphenol											
Ethylphenol											
C_3 phenol											
Fluorene							32				
Methyl Fluorene						+	+				
C_2 Fluorene											
Indole							76				
Methyl Indole	5						125				
C_2 Indole							+				
Dibenzothiophene						15	5				
Methyl Dibenzothiophene						12	9				
Methyl Dihydroindene	2					9					
C_2 Dihydroindene	4					16					
Benzoic Acid											
Ethyl Isothiocyanate											
Cyclohexylamine											

(continued)

TABLE 26 (continued)

Compound	# ISO	MMF-AC BN	MMG-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Butoxyethanol											
Aniline											
Toluidine											
Nitrosocarbazole											
Dibenzofuran							+				
Benzofluorene											
C_{12}						7					
C_{13}						15					
C_{14}						28					
C_{15}						60					
C_{16}						72					
Pristane						18					
C_{17}						76					
C_{18}					+	76					
Phytane					+						
C_{19}					+	63					
C_{20}					+	44					
C_{21}						28					
C_{22}						+					

(continued)

TABLE 26 (continued)

Compound	# ISO	MMF-AC BN	MMG-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
C_{23}						+					
C_{24}						+					
C_{25}						+					
Methyl Carbazole	4						285				
C_2 Carbazole	9						292				
C_3 Carbazole							+				
Acetic Acid											
Butyric Acid											
Valeric Acid											
Chrysene/benzoanthracene											
C_2 Piperidine					+						
Carbazole							168				
C_{11}						4					
Xylene						+					
acenaphthene						+	+				
C_{26}						+	+				
Cyanobenzene											

(continued)

(Table 26 (continued)

Legend

+ = identified but not sufficient quantity to accurately quantify

ISO = number of isomers identified

MMF-AC = pilot scale mixed media filter-activated carbon unit

BP = full scale biopond treatment unit

SWS = sourwater stripper process unit

BN = base neutral extract

ACID = acid extract

HEX = hexane elution fraction from silica gel column clean-up of base neutral extract

BENZ = benzene elution fraction from silica gel column clean-up of base neutral extract

METH = methanol elution fraction from silica gel column clean-up of base neutral extract

VOL = volatile organics by nitrogen purge and trap on TENAX GC adsorbent, thermal desorbtion onto GC column

TTL = Total concentration of compound found in all fractions or extracts

TABLE 27. LIST AND CONCENTRATION (ug/l) OF SPECIFIC ORGANIC COMPOUNDS ISOLATED FROM REFINERY C WASTEWATER, 10-28-81

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Toluene											
Naphthalene											
Methyl Naphthalene	2					169	15				
Dimethyl Naphthalene	5					806	176				
Ethyl Naphthalene	2					74	33				
C_3 Naphthalene	10					1039	252				
C_4 Naphthalene	7					202	47				
Biphenyl											
Methyl Biphenyl	4					280	156				
Ethyl Biphenyl	6					215	158				
C_3 Biphenyl											
Diphenylethylene											
Anthracene/Phenan.						221	217				
Methyl (A/P)	4					129	473				
Ethyl (A/P)											
Dimethyl (A/P)	5					+	127				
C_3 (A/P)						+	+				

(continued)

TABLE 27 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Pyrene/fluoranthene						+	+				
Phenol											
Cresol											
Dimethylphenol											
Ethylphenol											
C_3 phenol											
Fluorene							38				
Methyl Fluorene	5					209	126				
C_2 Fluorene	3					+	84				
Indole							59				
Methyl Indole	3						91				
C_2-Indole	2										
Dibenzothiophene						+	28				
Methyl Dibenzothiophene	2					+	52				
Methyl Dihydroindene											
Dimethyl Dihydroindene						+					
Benzoic Acid											
Ethyl Isothiocyanate											
Cyclohexylamine											

(continued)

TABLE 27 (continued)

Compound	# ISO	NMF-AC BN	NMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Butoxyethanol											
Aniline											
Toluidine											
Nitrosocarbazole											
Dibenzofuran											
Benzofluorene											
C_{12}						37					
C_{13}						78					
C_{14}						140					
C_{15}						403					
C_{16}						2378					
Pristane						189					
C_{17}						606					
C_{18}						456					
Phytane						100					
C_{19}						417					
C_{20}						275					
C_{21}						151					
C_{22}						+					

(continued)

TABLE 27 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
C_{23}						+					
C_{24}						+					
C_{25}						+					
Methyl Carbazole	4						185				
C_2 Carbazole	2						12				
C_3 Carbazole							+				
Acetic Acid											
Butyric Acid											
Valeric Acid											
Chrysene											
Carbazole						+	150				
C_2 Acenaphthylene						376					
C_{11}						12					
Acenaphthylene						+					
Methyl Piperidine					+						
Thiacyclopentane					+						
Hexanedione					+						
Cyclohexeneone					+						
C_2 Piperidine					+						

TABLE 28. LIST AND CONCENTRATION (ug/l) OF SPECIFIC ORGANIC COMPOUNDS ISOLATED FROM REFINERY C WASTEWATERS, 11-2-81

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Toluene											
Naphthalene											
Methyl Naphthalene	5					93	210				
Dimethyl Naphthalene	6					641	1016				
Ethyl Naphthalene						156	127				
C_3 Naphthalene	13					1623	1603				
C_4 Naphthalene	9					1060	+				
Biphenyl											
Methyl Biphenyl	5				+	357	1487				
C_2 Biphenyl	3					174	342				
C_3 Biphenyl											
Diphenylethylene											
Anthracene/Phenan.						+	926				
Methyl (A/P)	4						1812				
C_2 (A/P)	8						1481				
C_3 (A/P)							+				

(continued)

TABLE 28 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	SP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Pyrene/fluoranthene							+				
Phenol											
Cresol											
Dimethylphenol											
Ethylphenol											
C_3 phenol											
Fluorene							81				
Methyl Fluorene	4					109	854				
C_2 Fluorene							+				
Indole							68				
Methyl Indole	4						119				
C_2-Indole							+				
Dibenzothiophene							126				
Methyl Dibenzothiophene							+				
Methyl Dihydroindene											
Dimethyl Dihydroindene						+					
Benzoic Acid											
Ethyl Isothiocyanate											
Cyclohexylamine											

(continued)

TABLE 28 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BU	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Butoxyethanol											
Aniline											
Toluidine											
Nitrosocarbazole											
Dibenzofuran											
Benzofluorene											
C_{12}						166					
C_{13}						245					
C_{14}						500					
C_{15}						846					
C_{16}					+	1672					
Pristane					+	274					
C_{17}					+	1376					
C_{18}					+	1250					
Phytane					+	214					
C_{19}					+	762					
C_{20}					+	766					
C_{21}					+	400					
C_{22}						+					

(continued)

TABLE 28 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
C_{23}						+					
C_{24}						+					
C_{25}						+					
Methyl Carbazole							165				
C_2 Carbazole							+				
C_3 Carbazole							+				
Acetic Acid											
Butyric Acid											
Valeric Acid											
Chrysene											
Acenaphthylene						+	85				
C_{10}						46					
C_{11}						99					
Carbazole							+				
C_2 Dibenzothiophene							+				
Hexanedione					+						
Cyclohexenone					+						
C_2 Piperidine					+						

TABLE 29. LIST AND CONCENTRATION (ug/L) OF SPECIFIC ORGANIC COMPOUNDS ISOLATED FROM REFINERY C WASTEWATERS, 11-9-81

Compound	# ISO	MEF-AC BN	MEF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TFL
Toluene		+					+				
Naphthalene						36					
Methyl Naphthalene	2					170	212				
Dimethyl Naphthalene	4				+	281	333				
Ethyl Naphthalene	2					46	83				
C_3 Naphthalene	12				+	209	284				
C_4 Naphthalene	5				+	78					
Biphenyl						+	+				
Methyl Biphenyl	4				+	107	99				
C_2 Biphenyl	2				+	+	64				
C_3 Biphenyl											
Diphenylethylene											
Anthracene/Phenan.						16	228				
Methyl (A/P)	4				+	28	310				
Dimethyl (A/P)					+						
C_3 (A/P)											

(continued)

TABLE 29 (continued)

Compound	# ISO	NMF-AC BN	NMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Pyrene/fluoranthene							+				
Phenol											
Cresol											
Dimethylphenol											
Ethylphenol											
C_3 phenol											
Fluorene						+	192				
Methyl Fluorene						11	99				
C_2 Fluorene											
Indole							82				
Methyl Indole	2						66				
C_2-Indole											
Dibenzothiophene						+	18				
Methyl Dibenzothiophene						+	+				
Methyl Dihydroindene						+	+				
Dimethyl Dihydroindene						+					
Benzoic Acid											
Ethyl Isothiocyanate											
Cyclohexylamine											

(continued)

TABLE 29 (continued)

Compound	# ISO	DMF-AC BN	DMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Butoxyethanol											
Aniline											
Toluidine											
Nitrosocarbazole											
Dibenzofuran							+				
Benzofluorene											
C_{12}						11					
C_{13}						21					
C_{14}						34					
C_{15}						68					
C_{16}						93					
Pristane					+	31					
C_{17}					+	94					
C_{18}					+	85					
Phytane					+	13					
C_{19}						81					
C_{20}						56					
C_{21}						33					
C_{22}						+					

(continued)

TABLE 29 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
C_{23}						+					
C_{24}						+					
C_{25}											
Methyl Carbazole	3						538				
C_2 Carbazole	6				+		854				
C_3 Carbazole							+				
Acetic Acid											
Butyric Acid											
Valeric Acid											
Chrysene											
Acenaphthylene							36				
Carbazole							338				
C_2 Dibenzothiophene						+					
C_{11}						+					
C_{10}						+					
Acenaphthene						+	+				
Methyl Dibenzofuran							+				
Dithiabutane					+						

(continued)

TABLE 29 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Hexanedione					+						
Cyclohexenone					+						
C_2 Piperidine					+						

TABLE 30. LIST AND CONCENTRATION (ug/l) OF SPECIFIC ORGANIC COMPOUNDS ISOLATED FROM REFINERY C WASTEWATERS, 11-16-81

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Toluene		+			+						
Naphthalene											
Methyl Naphthalene											
Dimethyl Naphthalene	4					5147	64				
Ethyl Naphthalene	2					1148					
C_3 Naphthalene	11					18924	243				
C_4 Naphthalene	10					6376					
Biphenyl											
Metlyl Biphenyl						736	32				
C_2 Acenephthene/biphenyl						4835	26				
C_3 Biphenyl											
Diphenylethylene											
Anthracene/Phenanthrene		+				1008	100				
Methyl (A/P)						4529	586				
Ethyl (A/P)											
Dimethyl (A/P)											
C_3 (A/P)											

(continued)

TABLE 30 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Pyrene/fluoranthene											
Phenol											
Cresol											
Dimethylphenol											
Ethylphenol											
C_3 phenol											
Fluorene											
Methyl Fluorene											
C_2 Fluorene											
Indole											
Methyl Indole							32				
C_2-Indole											
Dibenzothiophene											
Methyl Dibenzothiophene											
Methyl Dihydroindene							25				
Dimethyl Dihydroindene											
Benzoic Acid											
Ethyl Isothiocyanate											
Cyclohexylamine											

(continued)

TABLE 30 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
Butoxyethanol											
Aniline											
Toluidine											
Nitrosocarbazole											
Dibenzofuran											
Benzofluorene											
C_{12}						495					
C_{13}						124					
C_{14}						1940					
C_{15}						3608					
C_{16}						4148					
Pristane						2013					
C_{17}						4197					
C_{18}						2766					
Phytane						+					
C_{19}						3602					
C_{20}						1617					
C_{21}						908					
C_{22}											
C_{23}											

(continued)

TABLE 30 (continued)

Compound	# ISO	MMF-AC BN	MMF-AC ACID	BP ACID	BP BN	SWS HEX	SWS BENZ	SWS METH	SWS ACID	VOL	TTL
C_{24}											
C_{25}											
Methyl Carbazole							96				
C_2 Carbazole											
C_3 Carbazole											
Acetic Acid											
Butyric Acid											
Valeric Acid											
Chrysene											
C_{11}						231					
C_2 Acenaphthylene						1974	125				
C_3 Acenaphthylene							200				
Dithiabutane					+						
Morpholine					+						
Methyl Piperidine					+						
Cyclohexanone					+						
Methyl Thiobenzene					+						
C_3 Piperidine					+						
Methyl Sulfinyl Benzene											
Methyl Sulfonyl Benzene											

TABLE 31. OPERATING CONDITIONS AND CONCENTRATION OF ORGANICS IN SOUR WATER STRIPPER EFFLUENT DURING OZONE TREATMENT (RUN I)

Sour Water Stripper Effluent

Date of sample 9/14/81
Operating conditions
Temperature 150°F
Pressure 100 psig
Ozone dose rate (60 x 2.8 x 44.16) = 7420 mg/hr

Time (Hrs.)	Total Sample (l)	Sample Removed (l)	O_3 Dose Added (mg/l)	Total Applied O_3 Dose (mg/l)
12:05	12.56	--	.00	.00
12:35	12.56	.200	295.38	295.38
1:05	12.36	.120	300.16	595.18
1:35	12.24	.200	303.10	898.64
2:05	12.04	.120	308.14	1206.78
2:35	11.92	.200	311.24	1518.02
3:05	11.72	.120	316.55	1834.57
3:35	11.60	.200	319.83	2154.40
4:05	11.40	--	325.44	2479.84

Elapsed Time (Hrs.)	TOC (mg/l)	COD (mg/l)	COD/TOC	Dissolved O_3 (mg/l)	Off-gas O_3 (mg/l)
.00	386	1240	3.21	-	-
.50	-	-	-	.00	0.09
1.00	343	1010	2.95	-	-
1.50	-	-	-	3.25	0.62
2.00	285	656	2.30	-	-
2.50	-	-	-	6.40	0.13
3.00	245	506	2.07	-	-
3.50	-	-	-	9.22	3.54
4.00	167	335	2.00	-	-

Phenol
Initial N.A.
Final < .001 mg/l

Sulfide
Initial < 3 mg/l

Ozone Treatment of Sourwater Stripper Effluent

Samples of the sourwater stripper effluent were transported to the lab for ozonation. Two tests were performed at high pressure (100 psig) on effluent samples collected 9/14/81, Run I (Table 31) and Run II (Table 32). The percent removal of COD was 73% in run 1 and 74% in run 2. The percent removal of TOC was not as high, 57% and 56% in runs 1 and 2, respectively, as COD removals. The ratio of COD to TOC decreased from 3.21 at start of run to 2.00 at end. Ammonia concentration was analyzed in run 2 to determine if ammonia was creating a chemical oxygen demand. The concentration of ammonia was not significantly altered by ozone treatment (Table 32). Therefore, the shift in COD/TOC ration must indicate partial oxidation of hydrocarbons but not complete oxidation to carbon dioxide.

Two tests were performed at low pressure (8 psig) on effluent samples collected 10/8/81, Run III (Table 33) and Run IV (Table 34). The percent removal of COD was 56% in Run III and 57% in Run IV. As in Run I and II, the percent removal of TOC was less than that for COD, i.e. 35% in Run III and 46% in Run IV. The ratio of COD to TOC was also decreased. Phenol was completely oxidized by the ozone treatment at the end of four hours. The phenol concentration was monitored at 1 hour intervals in Run IV and revealed almost complete oxidation of phenol after 2 hours of treatment. No detectable levels of sulfides were found after ozone treatment.

The results clearly indicate ozonation could be used for reduction of COD, phenol, and sulfides in process wastewaters. Ozone treatment for 4 hours was not as effective as activated carbon or the biopond system in percent removal of TOC. Extension of time of treatment would probably improve percent removal of TOC by ozonation.

Based upon comparisons of percent removal of degradable organic contaminants, the pilot-scale mixed media filtration-activated carbon and lab scale ozonation unit could be utilized to treat concentrated process wastewaters from petroleum refineries. The full-sized biopond system at Refinery C achieved equivalent or better efficiencies in removal of COD, TOC, Oil and Grease, Phenol, Sulfides, and Ammonia than the pilot scale MMF-AC or lab-scale ozonation unit. We made no attempt to estimate capital costs of installation or operation costs of the units evaluated; however, it would appear that the biopond system would be more economical than either of the more advanced types of treatment systems. The MMF-AC or ozone treatment units might be more practical for addition to an existing refinery, where space to install a biopond system was not available.

TABLE 32. OPERATING CONDITIONS AND CONCENTRATION OF ORGANICS IN SOUR WATER STRIPPER EFFLUENT DURING OZONE TREATMENT (RUN II)

Date of sample 9/14/81

Operating conditions

Temperature 150°F

Pressure 100 psig

Ozone dose rate (60 x 2.8 x 49.34) = 8290 mg/hr.

Time (Hrs)	Total Sample (l)	Sample Removed (l)	O_3 Dose Added (mg/l)	Total Applied O_3 Dose (mg/l)
12:05	13.49	-	0.0	0.6
12:35	13.49	.200	307.26	307.26
1:05	13.29	.120	311.89	619.15
1:35	13.17	.200	314.73	933.88
2:05	12.97	.120	319.58	1253.46
2:35	12.85	.200	322.57	1576.03
3:05	12.65	.120	327.67	1903.70
3:35	12.53	.200	330.81	2234.51
4:05	12.33	-	336.17	2570.68

Elapsed Time (Hrs)	TOC (mg/l)	COD (mg/l)	COD/TOC	NH (mg/l as N)	Dissolved O_3 (mg/l)	Off-gas O_3 (mg/l)
0	416	1361	3.27	189	-	-
.50	-	-	-		0	0.42
1.00	340	1045	3.07	231	-	-
1.50	-	-	-		5.82	3.00
2.00	312	738	2.37	231	-	-
2.50	-	-	-		2.05	0.65
3.00	254	535	2.11	220	-	-
3.50	-	-	-		4.78	0.92
4.00	185	352	1.90	199	-	-

Phenol

Initial 191.3 mg/l

Final < .001 mg/l

Sulfide

Initial N.A.

TABLE 33. OPERATING CONDITIONS AND CONCENTRATION OF ORGANICS IN SOUR WATER STRIPPER EFFLUENT DURING OZONE TREATMENT (RUN III)

Date of sample 10/08/81
Operating conditions
Temperature 150°F
Pressure 8 psig
Ozone dose rate (60 x 2.8 x 53.11) = 8922 mg/hr

Time (hrs.)	Total Sample (l)	Sample Removed (l)	O_3 Dose Added (mg/l)	Total Applied O_3 Dose (mg/l)
12:20	12.72	-	.00	.00
12:50	12.72	.200	350.71	350.71
1:20	12.52	.200	356.31	707.02
1:50	12.32	.200	362.09	1069.11
2:20	12.12	.200	368.07	1437.18
2:50	11.92	.200	374.24	1811.42
3:20	11.72	.200	380.63	2192.05
3:50	11.52	.200	387.24	2579.29
4:20	11.32	.200	394.08	2973.37

Elapsed Time (hrs.)	TOC (mg/l)	COD (mg/l)	COD/TOC	Dissolved O_3 (mg/l)	Off-gas O_3 (mg/l)
.00	439	1453	3.31	-	-
0.50	-	-	-	8.43	0.18
1.00	389	1113	2.92	-	-
1.50	-	-	-	6.84	20.83
2.00	333	895	2.69	-	-
2.50	-	-	-	6.27	24.75
3.00	306	825	2.70	-	-
3.50	-	-	-	3.13	27.89
4.00	284	639	2.25	-	-

Phenol
Initial 187.8 mg/l
Final 0.018 mg/l

Sulfide
Initial < 3 mg/l

TABLE 34. OPERATING CONDITIONS AND CONCENTRATION OF ORGANICS IN SOUR WATER STRIPPER EFFLUENT DURING OZONE TREATMENT (RUN IV)

Date of sample 10/08/81
Operating conditions
Temperature 150°F
Pressure 8 psig
Ozone dose rate (60 x 2.8 x 55.34) = 9302 mg/hr.

Time (hrs.)	Total Sample (l)	Sample Removed (l)	O_3 Dose Added (mg/l)	Total Applied O_3 Dose (mg/l)
11:50	13.14	-	.00	.00
12:20	13.14	.200	353.96	353.96
12:50	12.94	.200	359.43	713.39
1:20	12.74	.200	365.07	1078.46
1:50	12.54	.200	370.89	1449.35
2:20	12.34	.200	376.90	1826.25
2:50	12.14	.200	383.11	2209.36
3:20	11.94	.200	389.21	2598.57
3:50	11.74	-	396.17	2994.74

Elapsed Time (hrs.)	TOC (mg/l)	COD (mg/l)	COD/ TOC	NH_3 (mg/l as N)	Phenol (mg/l)	pH	Dissolved O_3 (mg/l)	Off-gas O_3 (mg/l)
.00	426	1384	3.25	69.3	181.2	8.30	-	-
.50	-	-	-	-	-	-	2.15	0.72
1.00	353	1061	3.01	109.2	166.4*	4.25	-	-
1.50	-	-	-	-	-	-	3.55	2.85
2.00	312	828	2.65	92.4	0.2*	3.95	-	-
2.50	-	-	-	-	-	-	4.65	24.86
3.00	268	731	2.73	94.5	0.007*	4.65	-	-
3.50	-	-	-	-	-	-	3.09	27.23
4.00	230	597	2.60	95.5	0.1	4.95	-	-

Sulfide
Initial < 3 mg/l

(*) Analysis performed with smaller samples than normal.

Characterization of Residuals from Petroleum Refining

Residuals from selected process units in four petroleum refineries were analyzed by the EPA Extraction Procedure to determine if these waste products contained sufficient quantities of chemical contaminants to be classified as hazardous materials. The EPA Office of Solid Waste published guidelines defining hazardous materials based upon properties of ignitability, corrosivity, reactivity, and toxicity (Fed. Reg. 45:33084-33139). If the EP extract of a waste contained concentrations of contaminants in excess of those listed in the Federal Register (Table 35), it would be classified as hazardous and subject to special regulations for transport and disposal.

TABLE 35. MAXIMUM CONCENTRATION OF CONTAMINANTS FOR CHARACTERISTIC OF EP TOXICITY (Fed. Reg. 45:33122).

Contaminant	Max. Concentration, mg/l
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0
Endrin	0.02
Lindane	0.4
Methoxychlor	10.0
Toxaphene	0.5
2,4-D	10.0
2,4,5-TP Silvex	1.0

Five specific waste residuals from petroleum refining were listed as hazardous by EPA, dissolved air flotation (DAF), slop oil emulsions, heat exchanger bundle cleaning sludge, API separator sludge, and tank bottoms from leaded gasoline storage. We collected residuals from API separators at 4 refineries and samples of slop oil emulsion, dissolved air flotation, bottoms from light oil API separator, solids from a cooling tower blowdown, and sludges from an aerated bio-pond at 3 refineries. These samples were all extracted with the EPA Extraction Procedure and analyzed for selected chemical parameters to determine if the residuals would be classified as hazardous by EPA criteria.

The results were reported as weight/volume (mg/l) of EP extract in accordance with EPA protocol. In addition, we weighed aliquots of the residues so that the concentration of chemical contaminants could be converted to weight/weight (mg/kg) if so desired by the cooperating refineries (Table 36).

The results of the herbicide and chlorinated hydrocarbon pesticide analyses revealed no cases of the petroleum refinery residuals which exceeded EPA criteria (Tables 37 and 38). These results were not too surprising since these chemicals are not produced at the refineries and would occur in the residues only as a result of accidental misuse.

The concentration of mercury in the petroleum refinery residues analyzed was below detection limit (Tables 39, 40, 41, and 42).

The EP extracts from the oil refinery residuals were also analyzed for organic contaminants by extraction with methylene chloride at pH >11 and pH <2 to obtain a base-neutral and weak acid fraction, respectively. The base-neutral fraction was then separated into aliphatics, aromatics, and neutral compounds by silica gel chromatography. The aromatic fraction was analyzed by GC-MS to determine specific compounds which might occur in these residues. The number of compounds identified in the aromatic fractions ranged from zero in the cooling tower residues from Refinery C to 42 in the Refinery B slop oil emulsions (Table 43). The classes of hydrocarbon type compounds identified ranged from simple monocyclic aromatics such as toluene to complex polynuclear aromatics such as anthracene/phenanthrene. Some compound containing oxygen and sulfur substituents were also identified. The alkylated bicyclic and polycyclic aromatic compounds were most abundant in the extracts (Table 44).

TABLE 36. WET WEIGHT (g) OF SOLID RESIDUALS PROCESSED BY EPA EXTRACTION PROCEDURE

Sample	Weight
Refinery B Slop Oil	151.06
Refinery B DAF	150.11
Refinery B API	152.73
Refinery D #1	158.07
D12	203.50
A12	302.40
Refinery A Slop	100
Refinery A API	100
Refinery C Lt. Oil	100
Refinery C Master Separator	100
Refinery C Southplant Biopond	100
Refinery C Cooling Tower	100

TABLE 37. SUMMARY OF CONCENTRATION (ug/l) OF HERBICIDES IN EP EXTRACTS OF RESIDUALS FROM PETROLEUM REFINERIES

	2,4-D	2,4,5-T	Silvex
Refinery D Blank	<0.20	<0.06	<0.30
Refinery D - D12	<0.20	<0.06	<0.30
Refinery D - A12	<0.20	<0.06	<0.30
Refinery C Cooling Tower	<0.20	<0.06	<0.30
Refinery C Blank	<0.20	<0.06	<0.30
Refinery C Southplant Biopond	<0.20	0.17	<0.30
Refinery C Master Separator Set 2	<0.20	<0.06	<0.30
Refinery C Lt. Oil	<0.20	<0.06	<0.30
Refinery A Slop	<0.20	<0.06	0.84
Refinery API	<0.20	<0.06	<0.30
Refinery A Blank	<0.20	<0.06	<0.30

TABLE 38. SUMMARY OF CONCENTRATIONS (ug/l) OF CHLORINATED HYDROCARBON PESTICIDES IN EP EXTRACTS OF RESIDUALS FROM PETROLEUM REFINERIES

Sample Identification	a&b BHC	Lindane	Heptachlor	Aldrin	p,p DDE	Dieldrin	p,p DDT	Endrin	Methoxychlor	Chlordane	Arochlor 1254	p,p DDD
Ref. D - D12	55.56	10.00	<0.07	<0.07	<0.15	<0.25	<0.60	<0.70	<3.00	<6.00	<7.00	<0.50
Ref. D - A12	<0.09	<0.09	<0.07	<0.07	<0.15	<0.25	<0.60	<0.70	<3.00	<6.00	<7.00	<0.50
Ref. D Blank	<0.09	<0.09	<0.07	<0.07	<0.15	<0.25	<0.60	<0.70	<3.00	<6.00	<7.00	<0.50
Ref. A Blank	<0.09	<0.09	<0.07	<0.07	<0.15	<0.25	<0.60	<0.70	<3.00	<6.00	<7.00	<0.50
Ref. C Cooling Tower	<0.09	<0.09	<0.07	<0.07	0.98	<0.25	<0.60	<0.70	<3.00	<6.00	<7.00	<0.50
Ref. C Blank	<0.09	<0.09	<0.07	<0.07	<0.15	<0.25	<0.60	<0.70	<3.00	<6.00	<7.00	<0.50
Ref. C Southplant Biopond	<0.09	<0.09	<0.07	<0.07	<0.15	<0.25	<0.60	<0.70	<3.00	<6.00	<7.00	<0.50
Ref. C Master Separator Set 2	<0.09	<0.09	<0.07	<0.07	<0.15	<0.25	<0.60	<0.70	<3.00	<6.00	<7.00	<0.50
Ref. A Slop	<0.09	<0.09	<0.07	<0.07	<0.15	<0.25	<0.60	<0.70	<3.00	<6.00	<7.00	<0.50
Ref. C Lt. Oil	<0.09	<0.09	<0.07	<0.07	<0.15	<0.25	<0.60	<0.70	<3.00	<6.00	<7.00	<0.50
Ref. A API	<0.09	<0.09	<0.07	<0.07	<0.15	<0.25	<0.60	<0.70	<3.00	<6.00	<7.00	<0.50

TABLE 39. SUMMARY OF CONCENTRATIONS (mg/1) OF MAJOR CATIONS IN EP EXTRACTS OF RESIDUALS FROM REFINERY B

Sample Identification	Date	Na	Ca	Mg	K	Fe	Pb	Zn	Cu
API	7-17-82	17.44	381.44	19.08	15.26	41.94	0.745	4.71	0.59
DAF	" "	22.49	29.64	4.36	1.23	6.49	0.235	1.42	0.10
Slop Oil	" "	14.30	109.44	19.52	1.87	40.89	0.025	6.40	<0.04
Quality Control	EPA	46.6	5.3	8.4	2.1	0.60	0.08	0.20	0.25
Analysis	OSU	45.0	5.3	7.3	2.5	0.54	0.07	0.15	0.22

Sample Identification	Date	Cd	Ni	Cr	V	Se*	Hg	As*
API	7-17-82	<0.001	0.72	0.211	<0.005	0.08		<0.01
DAF	" "	3.250	0.31	0.887	0.009	<0.01		0.11
Slop Oil	" "	<0.001	1.10	0.305	0.006	<0.01		<0.01
Quality Control	EPA	0.0052	0.25	0.15	0.060	0.040	0.0090	0.04
Analysis	OSU	0.0056	0.22	0.14	0.054	0.032	0.0084	0.04

*EPA METHOD MANUAL SW-846 - STANDARD ADDITION

TABLE 40. SUMMARY OF CONCENTRATIONS (mg/l) OF MAJOR CATIONS IN EP EXTRACTS OF RESIDUALS FROM REFINERY A

Sample Identification	Date	Na	Ca	Mg	K	Fe	Pb	Zn	Cu
API	8-27-82	17.86	543.00	65.00	1.68	11.11	0.935	2.77	0.24
Slop Oil	" "	2.36	47.24	14.90	0.41	14.15	0.720	3.20	0.21
Quality Control	EPA	46.6	5.3	8.4	2.1	0.60	0.08	0.20	0.25
Analysis	OSU	45.0	5.3	7.3	2.5	0.54	0.07	0.15	0.22

Sample Identification	Date	Cd	Ni	Cr	V	Se*	Hg	As*
API	8-27-82	0.050	3.82	1.880	<0.005	<0.01	<0.0025	0.16
Slop Oil	" "	<0.001	0.70	3.033	0.019	<0.01	<0.0025	0.05
Quality Control	EPA	0.0052	0.25	0.15	0.060	0.040	0.0090	0.03
Analysis	OSU	0.0056	0.22	0.14	0.054	0.032	0.0084	0.04

*EPA METHOD MANUAL SW-846 - STANDARD ADDITION

TABLE 41. SUMMARY OF CONCENTRATIONS (mg/l) OF MAJOR CATIONS IN EP EXTRACTS OF RESIDUALS FROM REFINERY C

Sample Identification	Date	Na	Ca	Mg	K	Fe	Pb	Zn	Cu
Bio. Pond	8-9-82	6.43	6.76	1.24	0.45	5.32	0.755	0.58	0.30
Cooling Tower	" "	31.55	237.54	38.00	3.20	81.53	1.091	27.62	0.14
API	" "	32.30	1099.54	56.00	1.61	52.23		5.92	<0.04
Master Sep.	" "	21.18	961.54	38.00	1.74	18.68	3.010	5.08	0.25
Quality Control	EPA	46.6	5.3	8.4	2.1	0.60	0.08	0.20	0.25
Analysis	OSU	45.0	5.3	7.3	2.5	0.54	0.07	0.15	0.22

Sample Identification	Date	Cd	Ni	Cr	V	Se*	Hg	As*
Bio. Pond	8-9-82	0.010	16.49	0.021	<0.005	<0.01	<0.0025	<0.01
Cooling Tower	" "	<0.001	3.20	4.522	0.005	<0.01	<0.0025	0.09
API	" "	0.008	14.50	0.467	<0.005	0.70	<0.0025	0.05
Master Sep.	" "	<0.001	11.51	0.206	0.009	<0.01	<0.0025	0.10
Quality Control	EPA	0.0052	0.25	0.15	0.060	0.040	0.0090	0.04
Analysis	OSU	0.0056	0.22	0.14	0.054	0.032	0.0084	0.04

* EPA METHOD MANUAL SW-846 - STANDARD ADDITION

TABLE 42. SUMMARY OF CONCENTRATIONS (mg/1) OF MAJOR CATIONS IN EP EXTRACTS OF RESIDUALS FROM REFINERY D

Sample Identification	Date	Na	Ca	Mg	K	Fe	Pb	Zn	Cu
API	10-82	28.47	1346.65	106.00	4.65	0.40	<0.025	4.30	<0.04
DAF	" "	111.41	17.08	27.77	30.59	19.48	<0.025	16.79	<0.04
Quality Control	EPA	46.6	5.3	8.4	2.1	0.60	0.08	0.20	0.25
Analysis	OSU	45.0	5.3	7.3	2.5	0.54	0.07	0.15	0.22

Sample Identification	Date	Cd	Ni	Cr	V	Se*	Hg	As*
API	10-82	<0.001	2.74	<0.010	<0.005	<0.01	<0.0025	<0.01
DAF	" "	<0.001	2.25	1.117	<0.005	<0.01	<0.0025	0.07
Quality Control	EPA	0.0052	0.25	0.15	0.060	0.040	0.0090	0.04
Analysis	OSU	0.0056	0.22	0.14	0.054	0.032	0.0084	0.04

* EPA METHOD MANUAL SW-846 - STANDARD ADDITION

TABLE 43. SUMMARY OF NUMBERS AND CLASSES OF ORGANIC COMPOUNDS IDENTIFIED IN AROMATIC FRACTION OF BASE-NEUTRAL EP EXTRACTS FROM PETROLEUM REFINERY RESIDUALS

	Ref. B Slop	Ref. B DAF	Ref. B API	Ref. C Lt. Oil	Ref. C M.S.	Ref. C B.P.	Ref. A API	Ref. A Slop	Ref. D API	Ref. D D-12
Total # Compounds	42	35	31	28	22	4	33	34	37	40
	%	%	%	%	%	%	%	%	%	%
Monoaromatic	19	11	10	29	18	25	21	24	22	17
Bicyclic aromatic	33	32	22	36	36	-	40	35	35	40
PAH, <2 rings	33	43	52	21	36	-	30	29	30	30
Thio-aromatics	10	14	16	7	10	-	6	6	8	8
Oxy-aromatics	5	-	-	7	-	25	3	6	5	5
Nitrogen aromatics	-	-	-	-	-	50	-	-		

* No compounds were detected in Refinery C cooling tower or Refinery D A12. Detection limit 20 ug/l.

SUMMARY AND CONCLUSIONS

Phase I

Chemical characterization of selected process wastewaters from petroleum refineries indicated that contact waters from fluid catalytic cracking units, coking units, barometric condensors, and crude desalting units were major contributers of organic contaminants to refinery wastewaters. At Refinery A, where a reasonable estimate of wastewater volumes could be obtained, 4 process wastewater streams were responsible for greater than 60% of the phenol, sulfide, ammonia, BOD, TOC, and oil and grease contaminants which occurred in the combined wastewaters from the entire refinery. Either elimination of these process contact wastewaters by installation of equivalent non-contact units or intensive treatment of the process wastewaters would improve overall effluent quality from the refineries.

The occurence of selected types of organic compounds in the process wastewaters of the three refineries may have been related to either the fraction of the crude oil processed at the refinery, the type of refining process, or to the type of extraction procedure used in our lab to prepare the wastewater sample for analysis. The alkanes, cycloalkanes, alkyl aromatics, aromatics and polycyclic aromatics generally occurred in the same process wastewaters with a similarity coefficient of 0.60 to 1.00 (Figures 4, 5, and 6). Also the more polar phenolic and acidic compounds tended to occur in the same process wastewaters (Figures 4, 5, and 6). This tendency should be investigated over a broader spectrum of process wastewaters from more refineries. If this is a true tendency for composition of petroleum process wastewaters and not an anomalous distribution imposed by the sample preparation and analysis procedures, it could be extremely valuable in isolating process wastewaters which contribute most of the problem "priority" organic contaminants. For example, there were 36 aromatic, alkyl aromatic, and poly cyclic aromatic compounds with a similarity coefficient of greater than 0.60 occuring in process wastewaters of the three different refineries. Most of these compounds occurred in the process wastewater from the sour water stripper and some other process wastewater streams such as cautic neutralizer and barometric condensor. Many refineries have already recognized the high level of hydrocarbon contamination in the stripped sour water and routinely recycle and reuse this water in the crude desalting process. This practice probably decreases level of hydrocarbon contamination by solubility partitioning of the hydrocarbons back into the crude oil. However, most refineries currently discharge this process wastewater into the combined wastewater treatment plant. The conventional secondary bio-oxidation wastewater treatment plant may not be adequate to reduce levels of these priority organic pollutants to a "biologically" safe level.

A comparison of similarity was performed by a Pinkham and Pearson coefficient of association between specific organic compounds and concentration of cations analyzed in the process wastewaters. A dendographic presentation illustrated similarity in composition of organic compounds between the barometric condenser effluent, coker plant effluent and influent to the sour water stripper at Refinery A (Figure 7). The effluent from the sour water stripper was more similar to the final effluent than to the other

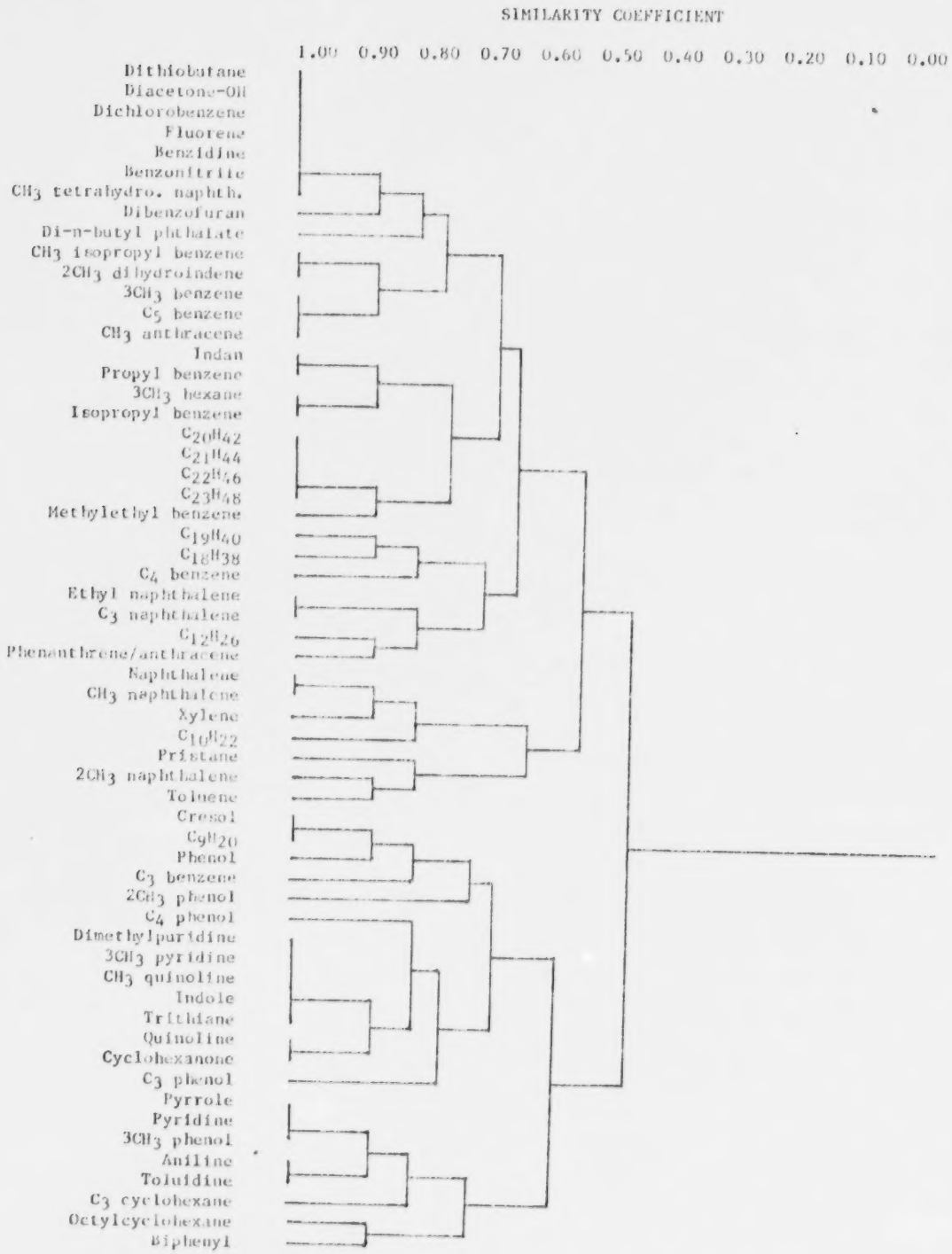


Figure 4. Dendogram plot of Pinkham and Pearson coefficient of association of organic compounds identified in Refinery A process wastewater streams.

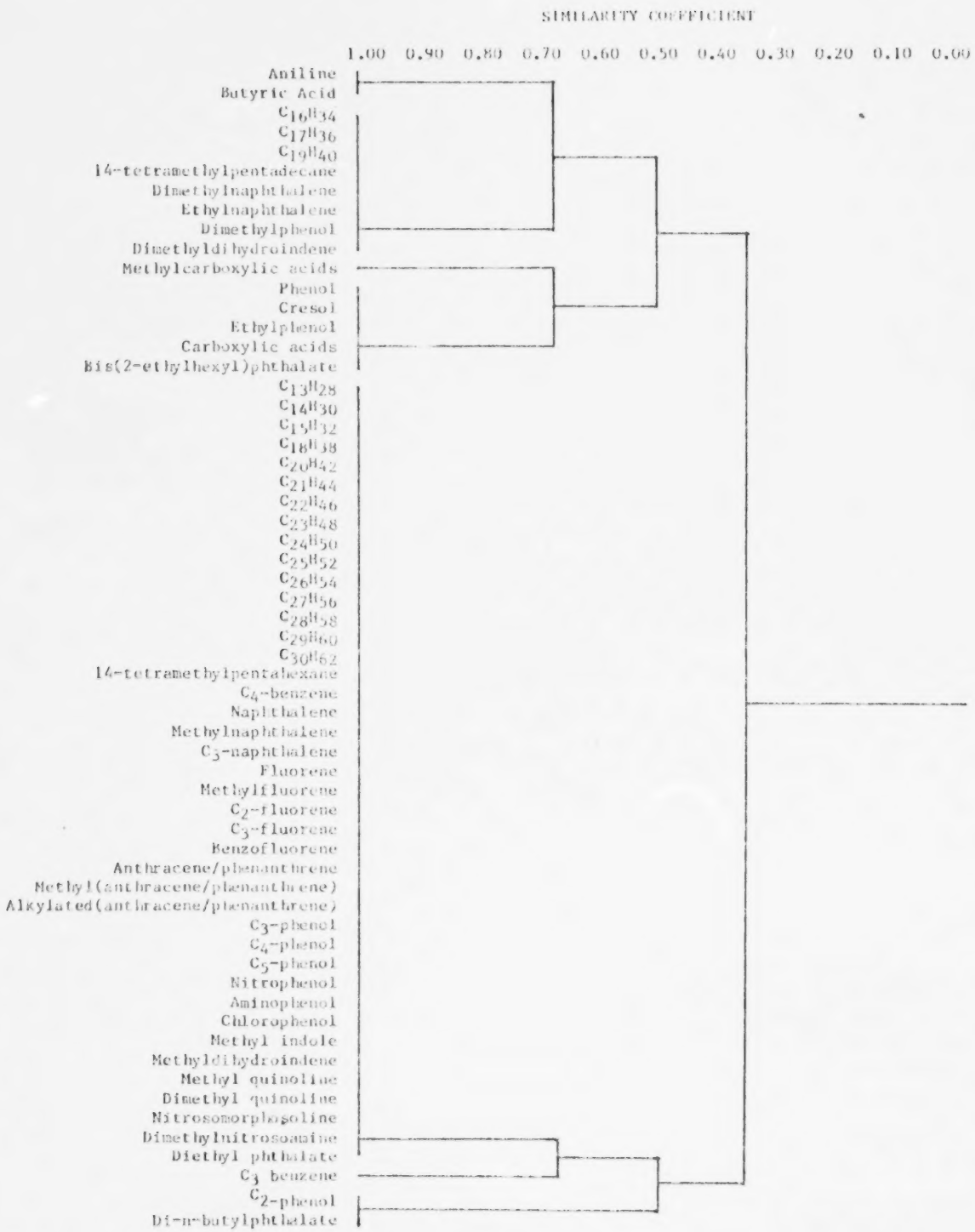


Figure 5. Dendogram plot of Pinkham and Pearson coefficient of association of organic compounds identified in Refinery B process wastewaters.

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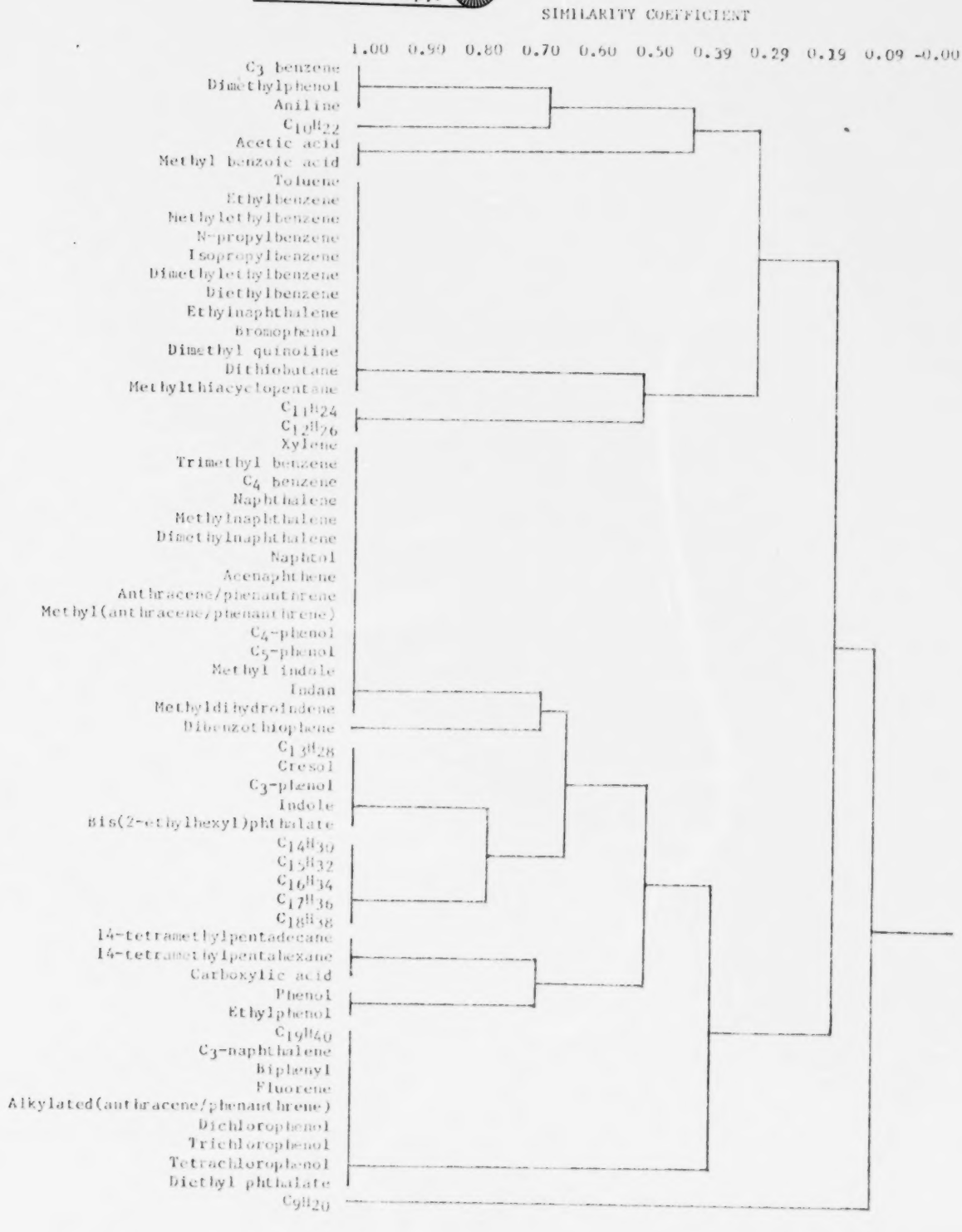

Figure 6. Dendogram plot of Pinkham and Pearson coefficient of association of organic compounds identified in Refinery C process wastewaters.

process wastewaters. The specific organic compounds identified in the sour water stripper effluents were not very similar to those identified in the API trap effluents at Refineries B and C (Figure 7).

In contrast, the same similarity coefficients indicated that the final effluent was most similar to the caustic neutralizer effluent with respect to concentrations of heavy metals at Refinery A (Figure 8). The coker effluent was the most unique and the influent and effluents of the sour water stripper had the highest degree of similarity at Refinery A.

Phase II

The percentage removal efficiency of the full-scale biopond system at Refinery C for conventional pollutant parameters such as phenol, sulfide, BOD, TOC, and oil and grease was greater than 90%. While not as efficient as the pilot scale mixed media filter-activated carbon treatment system during initial stages, i.e. greater than 95% removal, the biopond system achieved a better overall removal efficiency than the pilot scale MMF-AC. The adsorption capacity of the pilot scale carbon columns for TOC was exceeded by second day during the second on-site test. However, break-through of phenol did not occur until the 16th day of the test. The biopond system appeared to be comparable to the MMF-AC system from an overall viewpoint.

Laboratory evaluations of the capability of ozonation to reduce organic pollutant loads in concentrated process wastewaters indicated that greater than 73% removal of COD could be achieved within 4 hours of treatment at 100 psig. Low pressure (8 psig) ozonation achieved greater than 56% removal of COD within 4 hours of treatment.

The on-site scale and laboratory evaluations showed that advanced type of treatment systems could be used to reduce total concentration of organic pollutants from highly contaminated process wastewaters. However, these systems would not be as practical or economically feasible as biological oxidation units.

Phase III

Chemical characterization of EP extracts from selected petroleum refinery residuals indicated that the residuals analyzed would not be classified as "toxic" by EPA's criteria. Based upon the results of this project, it would appear that API separator residuals, and possibly DAF and slop oil emulsions, should not be categorically listed as hazardous wastes but should be analyzed on a case by case basis. Admittedly, the number of petroleum refinery residuals sampled during this project was too few to permit us to determine that these residuals are generally not hazardous. However, sufficient samples were analyzed to determine that not all API separator residuals should be categorically classified as hazardous.

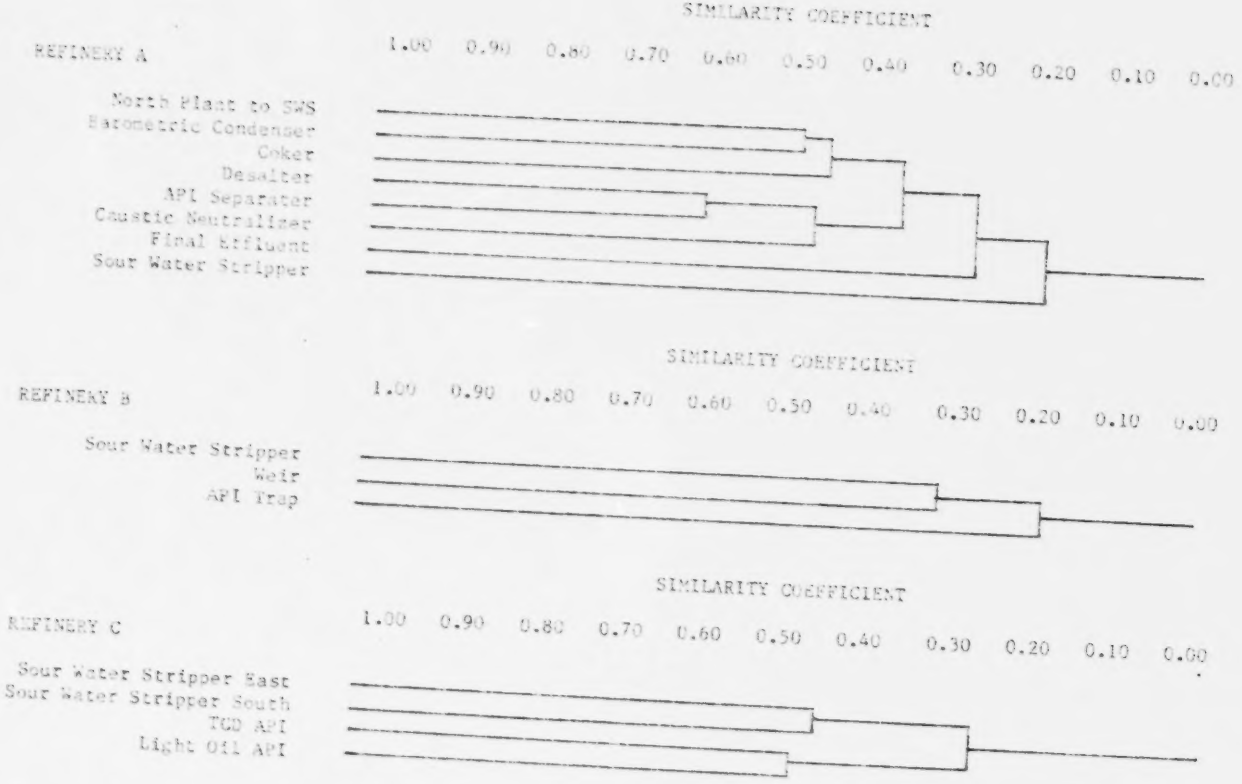

Figure 7. Dendogram plot of Pinkham and Pearson coefficient of association of similarity of process wastewaters with respect to organic contaminants.

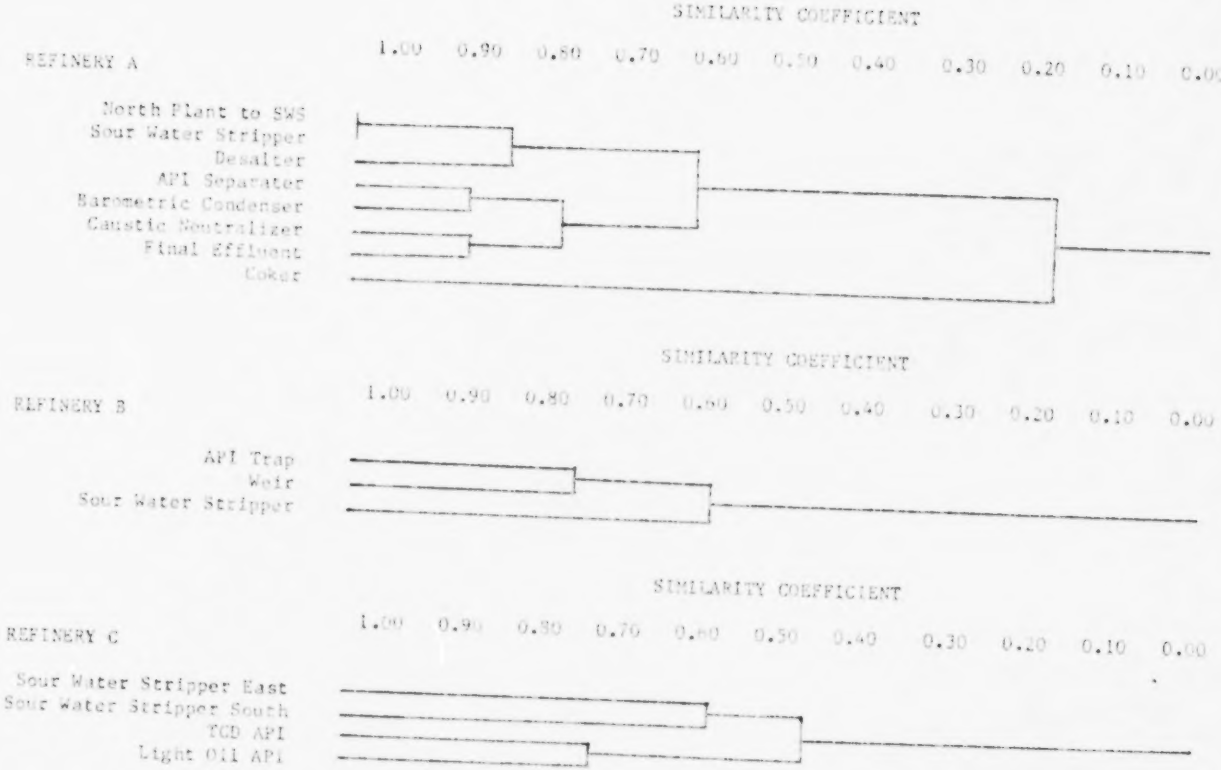

Figure 8. Dendogram plot of Pinkham and Pearson coefficient of association of similarity of process wastewaters with respect to heavy metal contaminants.

The overall results of the three phases of this project clearly indicate the complexity of petroleum refinery wastewaters and residuals. Application of the high resolution capacity of capillary chromatography coupled with identification capabilities of mass spectrometry resulted in a bewildering list of specific organic contaminants identified in the petroleum refinery process wastewaters. The significance of some of the compounds identified is difficult to ascertain, at this time. Perhaps the most significant finding was the absence of detectable quantities of "priority" pollutants in biologically treated refinery wastewaters, thus illustrating the effectiveness of biodegradation processes for removal of most of these hazardous organic contaminants or at least reduction of concentrations to non-deleterious levels.

TABLE 44. CONCENTRATION (ug/l) OF SPECIFIC ORGANIC COMPOUNDS IDENTIFIED IN EP EXTRACTS FROM PETROLEUM REFINING RESIDUALS.

Sample	Ref. B API	Ref. B Slop	Ref. B DAF	Ref. C Light oil	Ref. C Biopond	Ref. C cooling tower*
Toluene	2724	5779	5721	4765	2208	
Xylene		101	53	56		
Trimethyl benzene	63	312	110	167		
Methylethyl benzene		96		25		
Methyl propylbenzene		60		<10		
Dimethyl ethyl benzene		208		40		
Tetramethyl benzene	43	288	240	229		
C5-benzene		1156		54		
Benzaldehyde					73	
Dihydroindene		35		<10		
Methyl dihydroindene	95	38				
C_2 dihydroindene		605				
Naphthalene	150	1611	322	141		
Methyl naphthalene	1195	9828	2584	429		
Dimethyl naphthalene	3188	15978	5352	750		

(continued)

* Nothing present in these above detection levels 20 ug/l.

TABLE 44 (continued)

Sample	Ref. C Master Separator	Ref. D API	Ref. A API	Ref. A Slop	A12*	D12
Toluene	5744	314		13321		
Xylene	<10	152	113	283		1533
Trimethyl benzene	13	380	130	528		2448
Methylethyl benzene		98	44	193		696
Methyl propylbenzene		52	10	52		134
Dimethyl ethyl benzene		94	13	146		294
Tetramethyl benzene		677	103	88		1358
C5-benzene	<10	279	27	569		856
Benzaldehyde						
Dihydroindene		27	13	45		118
Methyl dihydroindene		65	25	334		816
C_2 dihydroindene		70	10			271
Naphthalene	<10	244	110	451		1316
Methyl naphthalene	25	1684	373	1640		10136
Dimethyl naphthalene	50	5516	661	2470		20840
Ethyl naphthalene	<10	496	72	200		1558
C_3 naphthalene	44	3944	575	2127		15464

(continued)

TABLE 44 (continued)

Sample	Ref. B API	Ref. B Slop	Ref. B DAF	Ref. C Light oil	Ref. C Biopond	Ref. C cooling tower
Ethyl naphthalene	572	1081	455	49		
C_3 naphthalene	2439	11729	4484	434		
C_4 naphthalene	837	1611	696	126		
C_5 naphthalene						
Tetrahydronaphthol		258		30		
Methyl tetrahydranaphthol						
Dimethyl tetrahydranaphthol				34		
Dimethyldihydronaphthalene		139				
Methyl alphatetralol		203				
Dimethyl thiaindene		82	108			
Biphenyl		559	183	57		
Acenaphthene		135	324			
Methyl (acenaphthene/biphenyl)	584	5108	1429	72		
C_2 (acenaphthene/biphenyl)		1579	498	24		
C_3 (acenaphthene/biphenyl)			457			
C_4 (acenaphthene/biphenyl)						
Fluorene	135	1252	258	84		

(continued)

TABLE 44 (continued)

Sample	DPQ Master Separator	Round Robin API	IPD API	IPD Slop	A12	D12
C_4 naphthalene						2554
C_5 naphthalene						
Tetrahydronaphthol		25	<10	76		172
Methyl tetrahydranaphthol						
Dimethyldihydronaphthalene		48	13	76		268
Methyl alpha tetralol		116	12	66		176
Dimethyl thiaindene		36				
Biphenyl	10	91	26	168		3477
Acenaphthene	15	39	28	89		842
Methyl (acenaphthene/biphenyl)	56	590	136	613		2270
C_2 (acenaphthene/biphenyl)		794	138	577		167
C_3 (acenaphthene/biphenyl)						335
C_4 (acenaphthene/biphenyl)						525
Fluorene	<10	131	27	356		1304
Methyl fluorene						1848
C_2 fluorene	<10	144	60	69		3042
C_3 fluorene	<10	22	30	42		771

(continued)

TABLE 44 (continued)

Sample	Ref. B API	Ref. B Slop	Ref. B DAF	Ref. C Light oil	Ref. C Biopond	Ref. C cooling tower
Methyl fluorene	763	1480	356			
C_2 fluorene	395	1176	972	15		
C_3 fluorene	109	522	581			
Naphthol thianaphthene	844		1312			
Methyl naphthol thianaphthene						
C_2 naphthol thianaphthene						
Dibenzothiophene	500	563	621	39		
Methyl dibenzothiophene	1000	1362	1618	25		
C_2 dibenzothiophene	2105	239	3725			
C_3 dibenzothiophene	818					
Anthracene/phenanthrene	3574	5142	6227	38		
Methyl (anthracene/phenanthrene)	13847	11640	21895	145		
C_2 (anthracene/phenanthrene)	16361	8596	22540	65		
C_3 (anthracene/phenanthrene)	5670	2228	4202	21		
C_4 (anthracene/phenanthrene)	1899		1435			
C_5 (anthracene/phenanthrene)	224					
Pyrene/fluoranthene	9432	1651	10156			

(continued)

TABLE 44 (continued)

Sample	Ref. C Master Separator	Ref. D API	Ref. A API	Ref. A Slop	A12	D12
Naphthol thianaphthene						
Naphthol thianaphthene						
Methyl naphthol thianaphthene						
C_2 naphthol thianaphthene						
Dibenzothiophene	20	520	105	268		1746
Methyl dibenzothiophene	17	304	76	210		1994
C_2 dibenzothiophene						1088
C_3 dibenzothiophene						
Anthracene/phenanthrene		251	174	365		4316
Methyl (anthracene/phenanthrene)	204	1042	458	860		11330
C_2 (anthracene/phenanthrene)	182	1233	593	667		7559
C_3 (anthracene/phenanthrene)	95	587		273		3750
C_4 (anthracene/phenanthrene)						252
Pyrene/fluoranthene	35	483	64			679
Methyl (pyrene/fluoranthene	66	1284	188	424		3718
C_2 (pyrene/fluoranthene)		290	68	157		
C_3 (pyrene/fluoranthene)						

(continued)

TABLE 44 (continued)

Sample	Ref. B API	Ref. B Slop	Ref. B DAF	Ref. C Light oil	Ref. C Biopond	Ref. C cooling tower
Methyl (pyrene/fluoranthene		2128	11471			
C_2 (pyrene/fluoranthene)	6038	510	6302			
C_3 (pyrene/fluoranthene)	16862					
Chrysene/benzanthracene	14900	1509	15260			
Methyl (chrysene/benzanthracene)	13836	354	9670			
C_2 (chrysene/benzanthracene)						
C_3 (chrysene/benzanthracene)						
Benzopyrene/benzofluoranthene)	22710	2864	11432			
Methyl (benzopyrene/ benzofluoranthene)						
C_2 (benzopyrene/benzofluoranthene)						
Indole					37	
Methyl indole					27	

(continued)

TABLE 44 (continued)

Sample	Ref. C Master Separator	Ref. D API	Ref. A API	Ref. A Slop	A12	D12
Chrysene/benzanthracene		351	144	460		2779
Methyl (chrysene/benzanthracene)						
C_2 (chrysene/benzanthracene)						
C_3 (chrysene/benzanthracene)						
Benzopyrene/benzofluoranthene)						
Methyl (benzopyrene/ benzofluoranthene)						
C_2 (benzopyrene/benzofluoranthene)						

TABLE A1. HEAVY METAL ANALYSIS - REFINERY C mg/l (ppm)

SAMPLE IDENTIFICATION	DATE	Na	Ca	Mg	K	Fe	Pb	Zn	Cu
Sour Water Stripper	9-14-81	25.1	15.4	6.4	1.0	0.27	<0.005	<0.05	<0.05
Bio Pond	"	147.2	55.9	9.6	5.6	0.79	<0.005	0.07	0.06
Act. Carbon	"	8.4	3.9	1.4	<1.0	<0.10	<0.005	0.05	<0.05
Quality Control Analysis	EPA	8.2	5.3	8.4	2.1	0.80	0.113	0.03	0.04
	OSU	8.4	8.7	10.0	2.0	0.72	0.095	0.04	0.04

SAMPLE IDENTIFICATION	DATE	Cr	V	Cd	Ni	Se	Hg	As
Sour Water Stripper	9-14-81	0.01	<0.005	<0.005	<0.1	0.11	<0.005	<0.05
Bio Pond	"	0.04	<0.005	<0.005	<0.1	0.40	<0.005	<0.05
Act. Carbon	"	<0.01	<0.005	<0.005	<0.1	<0.05	<0.005	<0.05
Quality Control Analysis	EPA	0.07	0.078	0.027	0.10	0.016	0.0076	0.06
	OSU	0.06	0.085	0.027	0.11	0.014	0.0069	0.08

TABLE A2. HEAVY METAL ANALYSIS - REFINERY C mg/1 (ppm)

SAMPLE IDENTIFICATION	DATE	Na	Ca	Mg	K	Fe	Pb	Zn	Cu
Sour Water Stripper	9-22-81	26.4	12.6	2.1	1.0	0.12	<0.005	<0.05	<0.05
Bio Pond	"	194.3	59.4	7.5	5.6	0.20	<0.005	<0.05	<0.05
Act. Carbon	"	25.4	1.4	<1.0	<1.0	<0.10	<0.005	0.09	<0.05
Quality Control Analysis	EPA	8.2	5.3	8.4	2.1	0.80	0.030	0.48	0.37
	OSU	7.6	8.3	8.2	2.0	0.75	0.031	0.43	0.37

SAMPLE IDENTIFICATION	DATE	Cr	V	Cd	Ni	Se	Hg	As
Sour Water Stripper	9-22-81	<0.01	<0.005	<0.005	<0.1	0.10	<0.005	<0.05
Bio Pond	"	0.02	<0.005	<0.005	<0.1	0.36	<0.005	<0.05
Act. Carbon	"	<0.01	<0.005	<0.005	<0.1	<0.05	<0.005	<0.05
Quality Control Analysis	EPA	0.06	0.078	0.027	0.10	0.05	0.008	0.06
	OSU	0.06	0.085	0.027	0.11	0.04	0.008	0.08

TABLE A3. HEAVY METAL ANALYSIS - REFINERY C mg/l (ppm)

SAMPLE IDENTIFICATION	DATE	Na	Ca	Mg	K	Fe	Pb	Zn	Cu
Sour Water Stripper	9-28-81	44.7	22.8	3.4	1.4	0.19	<0.005	<0.05	<0.05
Bio Pond	"	190.4	54.7	7.2	5.4	0.30	<0.005	<0.05	<0.05
Act. Carbon	"	87.0	<1.0	<1.0	5.3	0.27	<0.005	<0.05	<0.05
Quality Control Analysis	EPA	8.2	5.3	8.4	2.1	0.80	0.030	0.48	0.37
	OSU	7.6	8.3	8.2	2.0	0.75	0.031	0.43	0.37

SAMPLE IDENTIFICATION	DATE	Cr	V	Cd	Ni	Se	Hg	As
Sour Water Stripper	9-28-81	0.03		<0.005	<0.1	<0.05	<0.005	<0.05
Bio Pond	"	0.05		<0.005	<0.1	0.22	<0.005	<0.05
Act. Carbon	"	<0.01		<0.005	<0.1	0.71	<0.005	<0.05
Quality Control Analysis	EPA	0.07		0.027	0.10	0.05	0.008	0.06
	OSU	0.06		0.027	0.11	0.04	0.008	0.08

TABLE A4. HEAVY METAL ANALYSIS - REFINERY C mg/l (ppm)

SAMPLE IDENTIFICATION	DATE	Na	Ca	Mg	K	Fe	Pb	Zn	Cu
Sour Water Stripper	10-5-81	68.1	34.6	5.2	2.4	0.52	<0.005	0.32	0.06
Bio Pond	"	137.2	56.2	7.7	5.1	0.14	<0.005	0.07	<0.05
Act. Carbon	"	58.4	7.4	4.6	1.8	<0.10	<0.005	<0.05	<0.05
Quality Control Analysis	EPA	8.2	5.3	8.4	2.1	0.80	0.030	0.48	0.37
	OSU	7.6	8.3	8.2	2.0	0.75	0.031	0.43	0.37

SAMPLE IDENTIFICATION	DATE	Cr	V	Cd	Ni	Se	Hg	As
Sour Water Stripper	10-5-81	0.07		<0.005	<0.1	0.10	<0.005	<0.05
Bio Pond	"	0.04		<0.005	<0.1	0.14	<0.005	<0.05
Act. Carbon	"	<0.01		<0.005	<0.1	0.07	<0.005	<0.05
Quality Control Analysis	EPA	0.07		0.027	0.10	0.05	0.008	0.06
	OSU	0.06		0.027	0.11	0.04	0.007	0.09

TABLE A5. HEAVY METAL ANALYSIS - REFINERY mg/l (ppm)

SAMPLE IDENTIFICATION	DATE	Na	Ca	Mg	K	Fe	Pb	Zn	Cu
Sour Water Stripper	10-8-81	57.6	14.6	4.37	2.6	0.63	<0.005	<0.05	<0.05
Bio Pond	"	123.1	43.3	7.52	4.7	0.34	<0.005	<0.05	<0.05
Act. Carbon	"	68.8	29.8	7.14	3.2	0.33	<0.005	<0.05	<0.05
Quality Control Analysis	EPA	46.6	30.1	1.8	2.1	0.80	0.030	0.48	0.04
	OSU	46.4	31.7	1.6	2.0	0.82	0.028	0.44	0.04

SAMPLE IDENTIFICATION	DATE	Cr	V	Cd	Ni	Se	Hg	As
Sour Water Stripper	10-8-81	0.09	<0.005	<0.005	<0.1	0.02	<0.005	<0.05
Bio Pond	"	0.05	<0.005	<0.005	<0.1	0.09	<0.005	<0.05
Act. Carbon	"	<0.01	<0.005	<0.005	<0.1	0.17	<0.005	<0.05
Quality Control Analysis	EPA	0.07	0.078	0.027	0.17	0.05	0.0076	0.06
	OSU	0.06	0.077	0.037	0.15	0.04	0.0078	0.08

TABLE A6. HEAVY METAL ANALYSIS - REFINERY C mg/l (ppm)

SAMPLE IDENTIFICATION	DATE	Na	Ca	Mg	K	Fe	Pb	Zn	Cu
Sour Water Stripper	10-26-81	51.4	11.8	2.4	1.5	0.46	<0.005	<0.05	0.11
Bio Pond	"	142.8	38.0	6.5	4.3	0.18	0.012	<0.05	<0.05
Act. Carbon	"	92.8	126.8	79.6	5.8	<0.10	0.013	<0.05	<0.05
Quality Control Analysis	EPA	46.6	30.1	1.8	2.1	0.80	0.030	0.48	0.04
	OSU	46.4	31.7	1.6	2.0	0.82	0.028	0.44	0.04

SAMPLE IDENTIFICATION	DATE	Cr	V	Cd	Ni	Se	Hg	As
Sour Water Stripper	10-26-81	0.06	<0.005	<0.005	<0.1	0.43	<0.0025	<0.05
Bio Pond	"	<0.01	0.011	<0.005	<0.1	0.26	<0.0025	<0.05
Act. Carbon	"	<0.01	<0.005	<0.005	<0.1	<0.05	<0.0025	0.09
Quality Control Analysis	EPA	0.07	0.078	0.027	0.17	0.05	0.0076	0.026
	OSU	0.06	0.077	0.037	0.15	0.03	0.0088	0.022

TABLE A7. HEAVY METAL ANALYSIS - REFINERY C mg/1 (ppm)

SAMPLE IDENTIFICATION	DATE	Na	Ca	Mg	K	Fe	Pb	Zn	Cu
Sour Water Stripper	10-28-81	4.2	2.5	<1.0	<1.0	0.28	0.014	<0.05	0.07
Bio Pond	"	150.0	16.6	5.6	4.0	0.45	<0.005	<0.05	<0.05
Act. Carbon	"	8.7	<1.0	<1.0	<1.0	<0.10	0.005	<0.05	<0.05
Quality Control Analysis	EPA	46.6	30.1	1.8	2.1	0.80	0.030	0.48	0.04
	OSU	46.4	31.7	1.6	2.0	0.82	0.028	0.44	0.04

SAMPLE IDENTIFICATION	DATE	Cr	V	Cd	Ni	Se	Hg	As
Sour Water Stripper	10-28-81	0.01	<0.005	<0.005	<0.1	0.95	<0.0025	<0.05
Bio Pond	"	0.04	<0.005	<0.005	<0.1	0.31	<0.0025	<0.05
Act. Carbon	"	<0.01	<0.005	<0.005	<0.1	0.84	<0.0025	<0.05
Quality Control Analysis	EPA	0.07	0.078	0.059	0.17	0.05	0.0076	0.026
	OSU	0.06	0.077	0.064	0.15	0.03	0.0080	0.022

TABLE A8. HEAVY METAL ANALYSIS - REFINERY C mg/l (ppm)

SAMPLE IDENTIFICATION	DATE	Na	Ca	Mg	K	Fe	Pb	Zn	Cu
Sour Water Stripper	11-2-81	53.6	12.0	2.7	1.8	<0.10	<0.005	0.05	<0.05
Bio Pond	"	103.8	25.4	4.2	3.1	<0.10	<0.005	<0.05	<0.05
Act. Carbon	"	54.8	2.9	1.3	1.7	<0.10	<0.005	<0.05	<0.05
Quality Control Analysis	EPA	46.6	30.1	1.8	2.1	0.80	0.030	0.48	0.04
	OSU	46.4	31.7	1.6	2.0	0.82	0.028	0.44	0.04

SAMPLE IDENTIFICATION	DATE	Cr	V	Cd	Ni	Se	Hg	As
Sour Water Stripper	11-2-81	<0.01	<0.005	<0.005	<0.1	0.55	<0.0025	<0.05
Bio Pond	"	<0.01	<0.005	<0.005	<0.1	0.44	<0.0025	<0.05
Act. Carbon	"	<0.01	<0.005	<0.005	<0.1	0.67	<0.0025	<0.05
Quality Control Analysis	EPA	0.07	0.078	0.059	0.17	0.05	0.0076	0.026
	OSU	0.06	0.077	0.064	0.15	0.03	0.0083	0.022

TABLE A9. HEAVY METAL ANALYSIS - REFINERY C mg/1 (ppm)

SAMPLE IDENTIFICATION	DATE	Na	Ca	Mg	K	Fe	Pb	Zn	Cu
Sour Water Stripper	11-9-81	1.2	1.9	<1.0	<1.0	<0.10	<0.005	<0.05	<0.05
Bio Pond	"	110.8	24.4	4.5	3.2	<0.10	<0.005	<0.05	<0.05
Act. Carbon	"	34.1	4.2	<1.0	1.5	<0.10	<0.005	<0.05	<0.05
Quality Control Analysis	EPA	46.6	30.1	1.8	2.1	0.80	0.030	0.48	0.04
	OSU	46.4	31.7	1.6	2.0	0.82	0.028	0.44	0.04

SAMPLE IDENTIFICATION	DATE	Cr	V	Cd	Ni	Se	Hg	As
Sour Water Stripper	11-9-81	0.02	<0.005	<0.005	<0.1	0.94	<0.0025	<0.05
Bio Pond	"	0.02	<0.005	<0.005	<0.1	0.43	<0.0025	<0.05
Act. Carbon	"	<0.01	<0.005	<0.005	<0.1	0.41	<0.0025	<0.05
Quality Control Analysis	EPA	0.07	0.078	0.059	0.17	0.05	0.0076	0.026
	OSU	0.06	0.077	0.064	0.15	0.03	0.0090	0.022

TABLE A10. HEAVY METAL ANALYSIS - REFINERY C mg/l (ppm)

SAMPLE IDENTIFICATION	DATE	Na	Ca	Mg	K	Fe	Pb	Zn	Cu
Sour Water Stripper	11-16-81	1.8	1.6	<1.0	<1.0	<0.10	<0.005	<0.05	0.06
Bio Pond	"	117.8	18.6	4.2	3.0	<0.10	<0.005	<0.05	<0.05
Act. Carbon	"	4.8	4.3	1.0	<1.0	<0.10	<0.005	<0.05	<0.05
Quality Control Analysis	EPA	46.6	30.1	1.8	2.1	0.80	0.030	0.48	0.04
	OSU	46.4	31.7	1.6	2.0	0.82	0.028	0.44	0.04

SAMPLE IDENTIFICATION	DATE	Cr	V	Cd	Ni	Se	Hg	As
Sour Water Stripper	11-16-81	0.02	<0.005	<0.005	<0.1	0.94	<0.0025	<0.05
Bio Pond	"	0.01	<0.005	<0.005	<0.1	0.37	<0.0025	<0.05
Act. Carbon	"	<0.01	<0.005	<0.005	<0.1	0.90	<0.0025	<0.05
Quality Control Analysis	EPA	0.07	0.078	0.059	0.17	0.05	0.0076	0.026
	OSU	0.06	0.077	0.064	0.15	0.03	0.0071	0.022